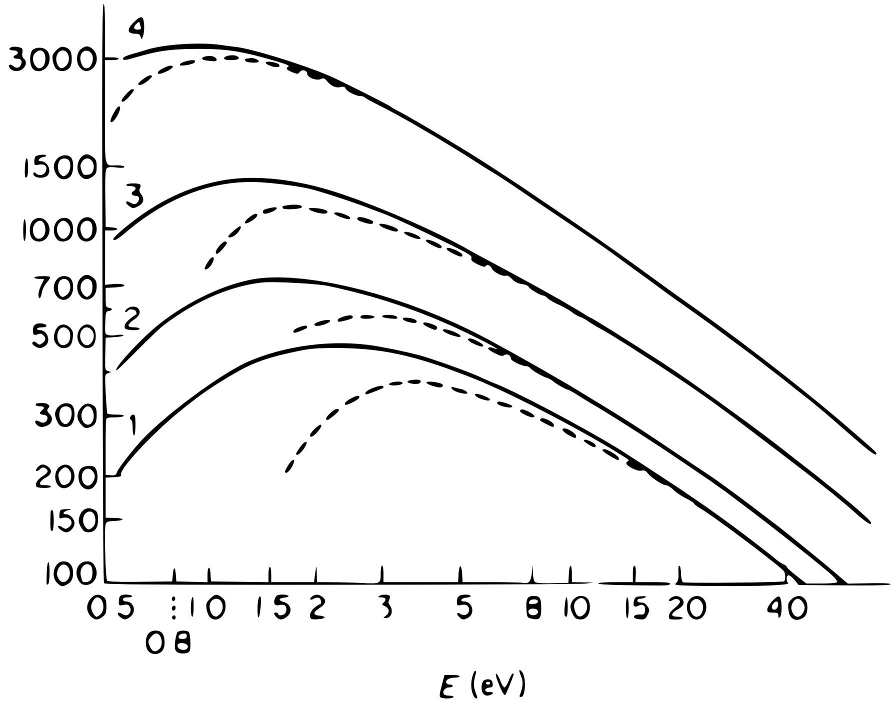
*G.F. Drukarev*

# THE THEORY OF ELECTRON-ATOM COLLISIONS



The Theory of

# Electron-Atom Collisions

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By

G. F. DRUKAREV

*Translated from the Russian by*
S. CHOMET

*Translation edited by*
J. B. HASTED

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## PREFACE TO RUSSIAN EDITION

THE theory of electron–atom collisions is given in many monographs, textbooks and reviews. The "Theory of Atomic Collisions" by Mott and Massey is the most substantial among these publications (the second edition was issued in 1950). Massey's articles "Theory of Atomic Collisions" and "Excitation and Ionization of Atoms by Electron Impact" in Handbuch der Physik (1956) are also concerned with this subject. Yu. N. Demkov's "Variatsionnye Printsipy v Teorii Stolknovenii" (1958) is devoted to variational methods.

However, the theory of atomic collisions has recently developed very rapidly in directions which are either not considered in these books or are only briefly mentioned. For example, substantial progress has been made in the application of dispersion relations to atomic collisions. Important results have been obtained on the extremal properties of the scattering length derived by variational methods. Computers have facilitated extensive calculations of scattering cross-sections with allowance for such factors as the polarization of the target atom by incident electrons, the coupling between different channels and so on. Calculations of this kind are being carried out at a very intensive rate both in the USSR and abroad. It has been found that the factors just mentioned are in many cases very important. The semi-classical theory of electron–atom collisions, first developed by Niels Bohr in connection with the interaction of fast particles with matter, has been developed still further.

The present book is largely devoted to recent developments in the theory of electron–atom collisions. It expounds both the general theory and its applications to specific problems. Chapters 1 and 2 are devoted to central force problems. The general theory of electron–atom collisions is discussed in Chapter 3 in the simplest case, i.e. the case of the hydrogen atom. Equations describing the collision of an electron with an arbitrary atom or ion are considered in Chapter 8. The remaining chapters are concerned with concrete calculations.

The general theory given in Chapters 3 and 8 is valid at any energy of the incident electrons, and covers both excitation and ionization processes. However, in concrete applications of the general theory we shall confine our attention to the interaction of slow electrons with atoms, i.e. elastic scattering at energies of a few electron volts, and inelastic scattering near the excitation threshold. It is precisely this energy range which is of the greatest interest in connection with the study of plasma processes and many other phenomena. On the other hand, approximate methods based on perturbation theory are not valid in this energy range, and a more complete analysis becomes necessary. For obvious reasons, most attention will be given to the interaction of electrons with the simplest systems, i.e. the hydrogen atom, the helium atom and the helium ion.

The account which we shall give of concrete calculations of collisions between electrons and the simple systems mentioned above is not intended to be exhaustive. We shall be mainly concerned with recent calculations in which the various complicating factors are taken into account. The results of some earlier papers will also be summarized. Ionization processes will not be considered.

I wish to thank Academician V. A. Fock, Yu. N. Demkov and L. D. Faddeev, whose comments have contributed to the improvement of this book.

*Leningrad* 1962 G. DRUKAREV

# PREFACE TO ENGLISH EDITION

As the study of atomic physics progresses, the scope of textbooks and monographs appears to become more limited, but correspondingly their depth increases. Editorial failure to understand and keep pace with this involution process would lead to a paucity of books which describe physical behaviour in sufficient detail or depth.

With depth of treatment in mind Professor Drukarev seeks only to discuss the quantum theory of electron–atom collisions, omitting detailed reference to other atomic and molecular collision processes. Since the 1949 edition of Mott and Massey's standard work "Theory of Atomic Collisions" few attempts have been made to cover the more general field, whilst all the time the subject has advanced, in principle, in magnitude and in refinement.

Important contributions to these advances have come from the University of Leningrad, where, under the aegis of V. A. Fock, Drukarev and others have concentrated their studies on electron collisions, developing the brilliant team who have established the neighbouring school at Riga.

"The Theory of Electron–Atom Collisions" should find a place not only with the professional quantum theorists but with those physicists who require merely to understand the effects produced by elastic and inelastic collisions, without personally manipulating the mathematics. No longer is it possible for the more classically inclined ionized gas physicist to aver that the quantum theory methods only nibble at the collision problem. Consider the achievements as of 1964: the ability to predict elastic scattering and excitation functions for simple atoms, with pointers in the direction of success for many-electron atoms; the prediction of the existence of virtual and real energy levels, and the scattering effects they produce; the establishment of upper limits with confidence which is far greater than that usually applied to theoretical cross-sections; the prediction of scattering cross-sections for electrons with ions and with excited atoms, collisions which have hardly yet been attempted in experiment. Only in ionizing collisions is the theoretical position rather less satisfactory.

The successes have come from such treatments as are described by Professor Drukarev: perturbation theory, distorted wave calculations, variational methods, allowances for exchange and for coupling, together with improved computational techniques.

All this has made it well worthwhile to undertake the translation into English of "The Theory of Electron–Atom Collisions", and a debt of gratitude is owing to Mr. Chomet for his capable efforts.

*November* 1964 J. B. HASTED

*University College London*

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*Chapter I*

# THE SCATTERING OF A PARTICLE BY A CENTRE OF FORCE

## 1. TIME-DEPENDENT THEORY OF SCATTERING

THERE are two ways of approaching the scattering of a particle by a centre of force. One of these is to be found in nearly all the existing textbooks of quantum mechanics; it involves the consideration of the continuous-spectrum wave function with a known asymptotic behaviour in a given field. This corresponds to the scattering of a stationary beam of particles with well-defined momentum at a large distance from the scattering centre, and represents an idealization of the real state of affairs.

The other approach is used in the time-dependent theory of scattering [1–5] and involves the study of the development of the process with time. Here one investigates the collision of a single particle with the centre of force rather than the scattering of a stationary beam of particles. The state of the particle is represented by a wave packet with a certain momentum distribution. This is closer to the conditions obtaining in real scattering experiments which nearly always involve the use of various collimating devices.

Any scattering experiment can be divided (somewhat schematically) into three parts: the formation of the state of the particle, its interaction with the centre of force, and finally, the determination of its state after the interaction. When the measuring and forming devices are at a large distance from the region of the interaction between the particle and the centre of force, the momentum distribution in the wave packet is independent of the distance traversed by the particle. We shall simplify the real conditions by assuming that the state of the particle is formed at time $t = -\infty$ while the final state determination is carried out at $t = +\infty$. A definite limiting momentum distribution will be supposed to exist in the wave packet as $t \to -\infty$ and $t \to +\infty$. The problem is then to establish the relation between the initial and final distributions.

The expressions for the scattering amplitude in terms of the wave functions are, of course, the same on either of the two approaches mentioned above. However, the time-dependent theory is in some respects more satisfactory. It is particularly advantageous in the case of scattering of a particle by a complicated system, for example an electron by an atom; and also in the analysis of the asymptotic behaviour of the wave function for the system along different directions in configuration space. The time-dependent treatment is also more convenient in the analysis of certain general problems.

We now proceed to the mathematical formulation of the theory, using the system of units in which $\hbar = m = 1$. In this system the dimensions of all the parameters can be reduced to the dimensions of length by multiplying them by the appropriate powers of $\hbar$ and $m$. For example, the total energy $E$ and potential energy $V$ of a particle have the dimensions of $[L]^{-2}$ when multiplied by $m/\hbar^2$. With a suitable choice of the scale of length it is possible to reduce all the parameters to a dimensionless form. The length characterizing the range of action of the field $V(r)$ is a natural unit of length. In the ensuing analysis of the scattering of an electron by an atom it will be convenient to take for it the Bohr radius $a_0$; the system of units is then known as the atomic system.

Let $\Phi(\boldsymbol{r}, t)$ be the wave function for the particle. In the atomic system of units it will satisfy the equation

$$i\frac{\partial\Phi}{\partial t} = H\Phi \tag{1.1}$$

where the energy operator $H$ may be written as the sum of the energy of free motion $H_0 = -\frac{1}{2}\Delta$ and the energy of interaction $V$ between the particle and the centre of force:

$$H = H_0 + V \tag{1.2}$$

We shall assume that $V$ is spherically symmetric and falls off with distance more rapidly than $r^{-1}$ as $r \to \infty$. The case $V \sim r^{-1}$ requires special consideration and is discussed in § 2.†

Let $\varphi_0$ be the eigenfunctions of the operator $H_0$ in the form

$$\varphi_0(E, \boldsymbol{v}, \boldsymbol{r}) = k^{\frac{1}{2}}(2\pi)^{-\frac{3}{2}}\, e^{ik\boldsymbol{v}.\boldsymbol{r}} \tag{1.3}$$

The plane wave $e^{ik\boldsymbol{v}.\boldsymbol{r}}$ describes the free motion of a particle with energy $E = \frac{1}{2}k^2$ and momentum $\boldsymbol{k} = k\boldsymbol{v}$. The normalizing factor $k^{\frac{1}{2}}(2\pi)^{-\frac{3}{2}}$ is chosen so that

$$\int \varphi_0^*(E', \boldsymbol{v}', \boldsymbol{r})\, \varphi_0(E, \boldsymbol{v}, \boldsymbol{r})\, d\boldsymbol{r} = \delta(E-E')\,\delta(\boldsymbol{v}-\boldsymbol{v}')$$

We expand $\Phi$ in terms of the eigenfunctions $\varphi_0$:

$$\Phi(\boldsymbol{r}, t) = \int e^{-iEt}\,\Psi_0(E, \boldsymbol{v}, t)\,\varphi_0(E, \boldsymbol{v}, \boldsymbol{r})\, dE\, d\Omega \tag{1.4}$$

We shall use the symbol $d\Omega$ to indicate integration with respect to angles over all the directions of the unit vector $\boldsymbol{v}$. This expansion represents the wave packet mentioned above. The description of a system with the aid of the function $\Psi_0$ is usually referred to as the interaction representation. On this particular representation the operator $H_0$ is diagonal. The function $\Psi_0(E, \boldsymbol{v}, t)$ is the state vector on the interaction representation. It is physically reasonable to assume that when $t \to -\infty$ there exists a definite limit of this function, which we shall denote by $\Psi_-$ (the function $\Phi(\boldsymbol{r}, t)$ has no limit when $t \to -\infty$). When $t \to +\infty$, the state vector $\Psi_0(E, \boldsymbol{v}, t)$ tends to a definite limit which we shall denote by $\Psi_+$. The existence of these limits reflects the fact that $\Phi(\boldsymbol{r}, t)$ satisfies the equation $i\partial\Phi/\partial t = H_0\Phi$ for a free particle when

---

† Some of the results given below are valid only when the requirements imposed on $V$ are more stringent. This will be pointed out at the appropriate places in our analysis.

$t \to -\infty$. The relation between the final state $\Psi_+$ and the initial state $\Psi_-$ may be expressed in the form

$$\Psi_+(E,v) = \int S(E,v,E',v')\Psi_-(E',v')\,dE'\,d\Omega' \tag{1.5}$$

The matrix $S$ which is defined by this relation is of fundamental importance in the theory of scattering. It follows from

$$\int |\Psi_+|^2\,dE\,d\Omega = \int |\Psi_-|^2\,dE\,d\Omega \tag{1.6}$$

that the $S$-matrix is unitary, that is,

$$\int S^*(E,v,E',v')\,S(E,v,E'',v'')\,\delta E\,d\Omega = \delta(E'-E'')\,\delta(v'-v'') \tag{1.7}$$

By considering the time-reversed motion, i.e. the situation when $t$ is replaced by $-t$ and $\Phi(t)$ by $\Phi^*(-t)$, it is possible to show that the $S$-matrix is symmetric with respect to time reversal; that is,

$$S(E,v,E',v') = S(E',-v',E,-v) \tag{1.8}$$

where the right-hand side corresponds to the time-reversed motion.

In order to obtain more detail about the structure of the $S$-matrix, let us consider the Heisenberg representation in addition to the interaction representation, and establish the relation between them.

Let $\varphi$ be the eigenfunction of the operator $H$ which satisfies the equation

$$H\varphi = E\varphi$$

or in another form

$$\Delta\varphi + (k^2 - 2V)\varphi = 0$$

We shall consider those functions $\varphi$ which have the asymptotic form:

$$\varphi_{r\to\infty} \sim \varphi_0 + O\left(\frac{1}{r}\right)$$

and are normalized to $\delta(E-E')\ \delta(v-v')$, as is $\varphi_0$. We shall see later that this does not define the function $\varphi$ unambiguously.

Let us expand $\Phi$ in terms of the functions $\varphi$:

$$\Phi(r,t) = \int e^{-iEt}\,\Psi(E,v)\,\varphi(E,v,r)\,dE\,d\Omega \tag{1.9}$$

where the right-hand side includes summation over the discrete spectrum. The function $\Psi$ is the state vector on the Heisenberg representation.

The relation between $\Psi_0$ and $\Psi$ is:

$$\Psi_0(E,v,t) = \int e^{-i(E'-E)t}\,w(E,v,E',v')\,\Psi(E',v')\,dE'\,d\Omega' \tag{1.10}$$

Comparison of the expansions (1.4) and (1.9) shows that

$$w(E,v,E',v') = \int \varphi_0^*(E,v,r)\,\varphi(E',v',r)\,dr \tag{1.11}$$

It will be convenient to transform (1.10) and (1.11) to another form. Let

$$\varphi = \varphi_0 + \chi \tag{1.12}$$

so that in view of (1.2) we have

$$(H-E)\chi = -V\varphi_0 \tag{1.13}$$

In order to write the solution of (1.13) in an operator form let us introduce the resolvent

$$\hat{G}(E) = (H-E)^{-1} \tag{1.14}$$

The operator $\hat{G}$ is uniquely defined for complex $E$, since in this case the operator $H-E$ has no zero eigenvalues. The ambiguity arises in the case of real $E$. If we regard $\hat{G}(E)$ as $\lim\limits_{\varepsilon\to+0} \hat{G}(E+i\varepsilon)$ then the result of the application of $\hat{G}$ will depend on the sign of $i\varepsilon$. It will be shown later that this sign, and therefore the resolvent itself (and thus the function $\varphi$ also), are unambiguously defined by specifying the initial condition for the state vector $\Psi_0(E, v, t)$ as $t \to -\infty$. When expressed in terms of the resolvent $\hat{G}$, the solution of (1.13) is of the form

$$\chi = -\hat{G}(E)V\varphi_0 \tag{1.15}$$

Substituting (1.15) into (1.12) we have

$$\varphi = \varphi_0 - \hat{G}V\varphi_0 \tag{1.16}$$

We can now employ the equation

$$\hat{G} = \hat{G}_0 - \hat{G}_0 V\hat{G} \tag{1.17}$$

which can be obtained from simple operator algebra. In this expression $\hat{G}_0$ is defined, analogous to $\hat{G}$, by the formula

$$\hat{G}_0 = (H_0 - E)^{-1} \tag{1.18}$$

Equation (1.16) can now be written

$$\varphi = \varphi_0 - \hat{G}_0 V\varphi \tag{1.19}$$

which is the integral equation for $\varphi$. Substituting (1.19) into (1.11) we have

$$w(E, v, E', v') = \delta(E-E')\,\delta(v-v') - \int \varphi_0^*(E, v, r,)\hat{G}_0(E')V(r)\,\varphi(E', v', r)\,dr \tag{1.20}$$

Since

$$\int \varphi_0^*\hat{G}_0 V\varphi\,dr = \int \varphi V(\hat{G}_0\varphi_0)^*\,dr$$

and also (for complex $E'$)

$$\hat{G}_0\varphi_0(E, v, r) = \frac{1}{H_0-E'}\varphi_0(E, v, r) = \frac{1}{E-E'}\varphi_0(E, v, r)$$

we can, using the substitution

$$T(E, v, E', v') = \int \varphi_0^*(E, v, r)\,V(r)\,\varphi(E', v', r)\,dr \tag{1.21}$$

rewrite equation (1.20) in the form

$$w(E, v, E', v') = \delta(E-E')\,\delta(v-v') - \frac{T(E, v, E', v')}{E-E'} \tag{1.22}$$

We note that this expression contains all the singularities of $w$ in an explicit form. The matrix $T(E, v, E', v')$ has no singularities at $E = E'$. If $V(r)$ falls off more rapidly than $r^{-3}$ when $r \to \infty$, then $T$ has no singularities when $v = v'$. It will be seen later that the matrix $T$ plays an important role, since the effective scattering cross-section can be expressed in terms of this matrix. We now substitute (1.22) into (1.10), giving

$$\Psi_0(E, v, t) = \Psi(E, v) - \int T(E, v, E', v') \frac{e^{-i(E'-E)t}}{E-E'} \Psi(E', v')\, dE'\, d\Omega' \tag{1.23}$$

In this expression $E$ is real and $E'$ complex. When $E'$ becomes real, there is a singularity in the integrand at the point $E = E'$. In order to establish the behaviour near this singularity, let us substitute the initial condition for $t = -\infty$. We shall require that when $t = -\infty$ the state vectors on the Heisenberg and on the interaction representations should be the same:

$$\Psi_0(E, v, -\infty) = \Psi(E, v) \tag{1.24}$$

In order to establish on this basis the contour of integration, let us transform (1.23) so that

$$\begin{aligned}\Psi_0(E, v, t) = \Psi(E, v) - \\ - \int \frac{T(E, v, E', v')\Psi(E', v') - T(E, v, E, v')\Psi(E, v')}{E-E'} e^{-i(E'-E)t} dE'\, d\Omega' - \\ - \int T(E, v, E, v')\Psi(E, v')\, d\Omega' \int\limits_C \frac{e^{-i(E'-E)t}}{E'-E} dE' \ldots\end{aligned} \tag{1.25}$$

The expression

$$Q = \frac{1}{E-E'}[T(E, v, E', v')\Psi(E', v') - T(E, v, E, v')\Psi(E, v')]$$

which enters into the first integral on the right-hand side of (1.25) exhibits no singularity at $E = E'$ and is integrable in the interval $0 \leqslant E' \leqslant \infty$. Therefore, from the Riemann-Lebesgue theorem we have

$$\lim_{t \to \pm\infty} \int_0^\infty Q\, e^{-iE't} dE' = 0$$

The integral

$$J = \int\limits_C \frac{e^{-i(E'-E)t}}{E'-E} dE'$$

tends to zero as $t \to -\infty$ if the contour of integration in the plane of complex $E'$ is chosen so that the point $E = E'$ is excluded, as shown in Fig. 1. In fact, assuming that for $t < 0$

$$-(E'-E)|t| = z$$

the integral $J$ may be transformed to read

$$J = \int_{-\infty}^{E|t|} \frac{e^{iz}}{z} dz$$

where the singularity at $z = 0$ is by-passed, as shown in Fig. 2. When $|t| \to \infty$ we have

$$J = \int_{-\infty}^{\infty} \frac{e^{iz}}{z} dz = 0$$

This method of excluding the singularity corresponds to the definition of the resolvents $\hat{G}$ and $\hat{G}_0$ as the limits

$$\hat{G}_0(E) = \lim_{\varepsilon \to +0} \hat{G}_0(E+i\varepsilon)$$

and

$$\hat{G}(E) = \lim_{\varepsilon \to +0} \hat{G}(E+i\varepsilon) \tag{1.26}$$

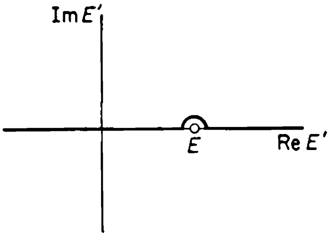

FIG. 1. Contour of integration in the $E'$-plane

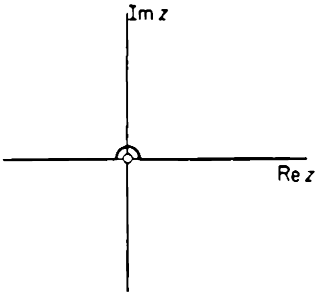

FIG. 2. Contour of integration in the $z$-plane

We can use the above limits, together with (1.14) and (1.18), to rewrite equation (1.16) in the form

$$\varphi = -\lim_{\varepsilon \to +0} i\varepsilon\hat{G}(E+i\varepsilon)\varphi_0 \tag{1.27}$$

We now consider the expression (1.25) in the limit $t \to \infty$. The first integral on the right-hand side vanishes as before in view of the Riemann-Lebesgue theorem. However, the integral

$$J = \int_C \frac{e^{-i(E'-E)t}}{E'-E} dE'$$

does not vanish as $t \to \infty$. Substituting $(E'-E)t = z$ when $t > 0$, we have

$$J = \int_{-Et}^{\infty} \frac{e^{-iz}}{z} dz$$

When $t \to \infty$ and the point $z = 0$ is excluded by deforming the contour of integration into a small circle above this point, we have $J = 2\pi i$. It follows that

$$\Psi_+ = \Psi_- - 2\pi i \int T(E, v, E', v') \Psi(E, v') \, d\Omega' \tag{1.28}$$

Comparison of (1.28) with (1.5) yields

$$S(E, v, E', v') = \delta(E - E')[\delta(v - v') - 2\pi i T(E, v, E, v')] \tag{1.29}$$

We have thus expressed the singularities of the $S$-matrix in an explicit form.

Let us now establish the connection between the effective scattering cross-section and the $T$-matrix [5]. We suppose that in the initial state the particle has a well-defined momentum near $k_0$ which is parallel to the $z$-axis and is localized in the volume $U$, so that $\psi = U^{-\frac{1}{2}} C \exp(ik_0 z)$, where $C = 1$ and

$$\left(-\frac{a_x}{2} \leqslant x \leqslant \frac{a_x}{2}\right), \quad \left(-\frac{a_y}{2} \leqslant y \leqslant \frac{a_y}{2}\right), \quad \left(-\frac{a_z}{2} \leqslant z \leqslant \frac{a_z}{2}\right)$$

$C = 0$ when at least one of the coordinates lies outside this interval. In momentum space the wave function will be of the form

$$\Psi_-(k) = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} U^{-\frac{1}{2}} \frac{\sin \frac{1}{2} k_x a_x}{k_x} \cdot \frac{\sin \frac{1}{2} k_y a_y}{k_y} \cdot \frac{\sin \frac{1}{2}(k_z - k_0) a_z}{k_z} \tag{1.30}$$

If we normalize along the energy scale, then

$$\Psi_-(E, v) = k \left(\frac{dk}{dE}\right)^{\frac{1}{2}} \Psi_-(k) \tag{1.31}$$

Let

$$\begin{aligned} \delta_a(\xi) &= \frac{1}{\pi} \frac{\sin \frac{1}{2} a\xi}{\xi} \\ \Delta_a(\xi) &= \left(\frac{2}{\pi a}\right)^{\frac{1}{2}} \frac{\sin \frac{1}{2} a\xi}{\xi} \end{aligned} \tag{1.32}$$

so that

$$\begin{aligned} \lim_{a \to \infty} \delta_a(\xi) &= \delta(\xi) \\ \lim_{a \to \infty} \Delta_a^2(\xi) &= \delta(\xi) \end{aligned} \tag{1.33}$$

Since $E = \frac{1}{2} k^2$ and $U = a_x a_y a_z$ we have

$$\Psi_-(E, v) = \left(\frac{k}{a_x a_y}\right)^{\frac{1}{2}} 2\pi \delta_{a_x}(k_x) \delta_{a_y}(k_y) \Delta_{a_z}(k_z - k_0) \tag{1.34}$$

Let $j$ be the particle current density in the initial wave packet. The cross-section of an arbitrary packet is $a_x a_y$, therefore the total flux of particles per unit time is

$$n_- = a_x a_y j \tag{1.35}$$

Next, the probability of finding a particle moving within the solid angle $d\Omega$ in the final state in the energy interval $dE$ is equal to

$$|\Psi_+(E, v)|^2\, dE\, d\Omega$$

Therefore, the number of particles which have been scattered per unit time into the solid angle $d\Omega$ within the energy interval $dE$ is

$$dn_+ = a_x a_y j |\Psi_+(E, v)|^2\, dE\, d\Omega \tag{1.36}$$

In view of (1.15) and (1.34),

$$dn_+ = j\left|2\pi \int S(E, v, E', v')\, \delta_{a_x}(k'_a)\, \delta_{a_y}(k'_y)\, \Delta_{a_z}(k'_z - k_0) \times \sqrt{k'}\, dE'\, d\Omega'\right|^2 dE\, d\Omega \tag{1.37}$$

Substituting (1.29) into this expression, we have, for $v \neq v'$,

$$dn_+ = (2\pi)^4 j \left| \int T(E, v, E, v')\, \delta_{a_x}(k'_x)\, \delta_{a_y}(k'_y)\, \Delta_{a_z}(k'_z - k_0) \times \delta(E - E')\sqrt{k'}\, dE'\, d\Omega'\right|^2 dE\, d\Omega \tag{1.38}$$

Consider the integral

$$J = \int T(E, v, E, v')\, \delta_{a_x}(k'_x)\, \delta_{a_y}(k'_y)\, \Delta_{a_z}(k'_z - k_0)\, \delta(E - E')\sqrt{k'}\, dE'\, d\Omega' \tag{1.39}$$

It will be convenient to replace integration with respect to $E'$ and $\Omega'$ by integration with respect to $k'_x$, $k'_y$ and $k'_z$, and replace $E'$ by $\frac{1}{2}(k'^2_x + k'^2_y + k'^2_z)$. The result of these substitutions is

$$J = \int T(E, v, E', v')\, \delta_{a_x}(k'_x)\, \delta_{a_y}(k'_y)\, \Delta_{a_z}(k'_z - k_0) \times \delta[E - \tfrac{1}{2}(k'^2_x + k'^2_y + k'^2_z)] \frac{1}{\sqrt{k'}}\, dk'_x\, dk'_y\, dk'_z \tag{1.40}$$

If it is supposed that $a_x$ and $a_y$ tend to infinity, we have (provided $|k'_z| = k'$)

$$J = \int_0^\infty T(E, v, E', v')\, \Delta_{a_z}(k' - k_0) \left(E - \frac{k'^2}{2}\right) \frac{dk'}{\sqrt{k'}} \tag{1.41}$$

and hence

$$J = k^{-\frac{1}{2}} T(E, v, E, v')\, \Delta_{a_z}(k - k_0) \tag{1.42}$$

On substituting (1.42) into (1.38) and taking the limit $a_z \to \infty$ in $\Delta_{a_z}$, we have, in view of (1.33),

$$dn_+ = j(2\pi)^4 |T(E, v, E, v')|^2\, \delta(k - k_0) k^{-3}\, dE\, d\Omega \tag{1.43}$$

When (1.43) is integrated over a small interval of energy in the final state, and the result denoted by $dN_+$, then

$$dN_+ = j(2\pi)^4 |T|^2 \frac{d\Omega}{k_0^2} \tag{1.44}$$

Hence, by definition of the effective cross-section $d\sigma$:

$$d\sigma = \frac{dN_+}{j} = \frac{(2\pi)^4}{k_0^2} \left| T(E, \mathbf{v}, E, \mathbf{v}') \right|^2 d\Omega \tag{1.45}$$

The total scattering cross-section can be obtained from this expression by integrating over all angles; the result is

$$\sigma = \frac{(2\pi)^4}{k_0^2} \int |T|^2 \, d\Omega \tag{1.46}$$

On substituting (1.29) into (1.7), and assuming that $\mathbf{v}'' = \mathbf{v}'$ then:

$$i[T(E, \mathbf{v}, E, \mathbf{v}) - T^*(E, \mathbf{v}, E, \mathbf{v})] = 2\pi \int \left| T(E, \mathbf{v}, E, \mathbf{v}') \right|^2 d\Omega' \tag{1.47}$$

or

$$-\operatorname{Im} T(0) = \pi \int |T|^2 \, d\Omega \tag{1.48}$$

where $T(0) = T(E, \mathbf{v}, E, \mathbf{v})$. The result (1.48) is known as the optical theorem. Finally, in view of (1.46) and (1.48):

$$-\frac{2^4 \pi^3}{k_0^2} \operatorname{Im} T(0) = \sigma \tag{1.49}$$

## 2. THE WAVE FUNCTION FOR A PARTICLE IN A CENTRAL FORCE FIELD

Let us now consider in detail the eigenfunction of the energy operator $H$ defined by equation (1.19) and the relation (1.26). It will be convenient to replace $\varphi$ by another function $\psi$ defined as

$$\psi(E, \mathbf{v}, \mathbf{r}) = (2\pi)^{\frac{3}{2}} k^{-\frac{1}{2}} \varphi(E, \mathbf{v}, \mathbf{r}) \tag{2.1}$$

In view of (1.3), (1.19) and (1.26) the integral equation for $\psi$ is

$$\psi = e^{ik\mathbf{v}.\mathbf{r}} - \lim_{\varepsilon \to +0} \hat{G}_0(E + i\varepsilon) V \psi \tag{2.2}$$

On the coordinate representation the resolvent is an integral operator centred upon a Green's function. The Green's function corresponding to the resolvent $\hat{G}_0(E + i\varepsilon)$ will be denoted by $G_0(\mathbf{r}, \mathbf{r}', E + i\varepsilon)$. In some cases we shall omit $E + i\varepsilon$ and write simply $G_0(\mathbf{r}, \mathbf{r}')$. This will be done whenever there is no danger of ambiguity. In this notation (2.2) may be rewritten in the form

$$\psi(\mathbf{r}) = e^{ik\mathbf{v}.\mathbf{r}} - \int G_0(\mathbf{r}, \mathbf{r}') \, V(\mathbf{r}') \, \psi(\mathbf{r}') \, d\mathbf{r}' \tag{2.3}$$

Let us determine the Green's function $G_0(\mathbf{r}, \mathbf{r}',)$ corresponding to the resolvent $\hat{G}_0(E + i\varepsilon)$. In the momentum representation:

$$G_0(\mathbf{r}, \mathbf{r}') = \lim_{\varepsilon \to +0} \frac{1}{(2\pi)^3} \int \frac{e^{ik'\mathbf{r}.\mathbf{v}'} \; e^{-ik'\mathbf{r}'.\mathbf{v}'} \, k'^2 \, dk' \, d\Omega'}{\frac{1}{2}k'^2 - (\frac{1}{2}k^2 + i\varepsilon)} \tag{2.4}$$

If we complete the integration with respect to $\Omega'$ and substitute

$$|\mathbf{r} - \mathbf{r}'| = \rho; \qquad k'\rho = z'; \qquad (k^2 + 2i\varepsilon)\rho^2 = z^2(\varepsilon) \tag{2.5}$$

we obtain

$$G_0 = \lim_{\varepsilon \to +0} \frac{1}{4\pi^2 \rho i} \left[ \int_{-\infty}^{\infty} \frac{e^{iz'} dz'}{z' - z(\varepsilon)} + \int_{-\infty}^{\infty} \frac{e^{iz'} dz'}{z' + z(\varepsilon)} \right] = \lim_{\varepsilon \to 0} \frac{1}{2\pi\rho} e^{iz} \tag{2.6}$$

and finally

$$G_0 = \frac{1}{2\pi |\boldsymbol{r} - \boldsymbol{r}'|} e^{ik|\boldsymbol{r} - \boldsymbol{r}'|} \tag{2.7}$$

Therefore the integral equation (2.2) becomes

$$\psi = e^{ik\boldsymbol{v}.\boldsymbol{r}} - \frac{1}{2\pi} \int \frac{e^{ik|\boldsymbol{r}-\boldsymbol{r}'|}}{|\boldsymbol{r}-\boldsymbol{r}'|} V\psi \, d\boldsymbol{r}' \tag{2.8}$$

For large $r$ the asymptotic behaviour of $\psi$ is

$$\psi \sim e^{ik\boldsymbol{v}.\boldsymbol{r}} + q(\boldsymbol{v}, \boldsymbol{n}) \frac{e^{ikr}}{r}, \qquad \text{where } \boldsymbol{n} = \frac{\boldsymbol{r}}{r} \tag{2.9}$$

and the amplitude $q$ is given by

$$q(\boldsymbol{v}, \boldsymbol{n}) = -\frac{1}{2\pi} \int e^{-ik\boldsymbol{n}.\boldsymbol{r}'} V\psi(\boldsymbol{v}, \boldsymbol{r}') \, d\boldsymbol{r}' \tag{2.10}$$

Comparison of (2.10) with (1.21) yields

$$q = -\frac{(2\pi)^2}{k} T(E, \boldsymbol{n}, E, \boldsymbol{v}) \tag{2.11}$$

With the aid of (2.11) and (1.45) we can express the effective cross-section in terms of $q$:

$$d\sigma = |q|^2 \, d\Omega \tag{2.12}$$

The optical theorem (1.48) may now be written in the form

$$\operatorname{Im} q(\boldsymbol{n}, \boldsymbol{n}) = \frac{k}{4\pi} \int |q(\boldsymbol{n}, \boldsymbol{v})|^2 \, d\Omega \tag{2.13}$$

The effective scattering cross-section given by (2.12) is obtained in the stationary theory by considering the asymptotic behaviour of the wave function (2.9). This is done by finding the current density associated with the scattered particles, i.e. with the term $q\, e^{ikr}/r$ in (2.9). This current density turns out to be equal to $k|q|^2$. The quantity $d\sigma/d\Omega$ which is equivalent to (2.12) is obtained by dividing this current density by the current density of the incident particles, which are described by the plane wave $\exp(ik\boldsymbol{v}.\boldsymbol{r})$. The latter current density is, of course, equal to $k$. The time-dependent theory provides the justification for this procedure. The expression (2.13) can also be obtained directly by considering the asymptotic form of the wave function (2.9). This can be done by setting the current through a sphere of arbitrary radius equal to zero, i.e.

$$\int (\psi \nabla \psi^* - \psi^* \nabla \psi) \, dS = 0$$

This condition represents the conservation of the number of particles on scattering.

Consider the wave function $\psi$ at $r = 0$. On setting $r = 0$ in (2.8) we have

$$\psi = 1 - \frac{1}{2\pi}\int e^{ikr'}\frac{1}{r'}V\psi\,d\boldsymbol{r}' \tag{2.14}$$

The second term in this expression is a measure of the distortion of the wave function at $r = 0$ due to the field $V(r)$. For large $k$ the value of this integral is small owing to the rapidly oscillating factors $\exp(ikr')$ and $\psi$. The maximum distortion occurs at $k = 0$. In the latter case (2.14) is of the form

$$\psi(0) = 1 - 2\int_0^\infty V(r')\psi(r')r'\,dr' \tag{2.15}$$

Applying the mean value theorem to $|\psi(0)-1|$ we obtain

$$\frac{|\psi(0)-1|}{\psi_m} = 2\int_0^\infty |V|r'\,dr' \tag{2.16}$$

where $\psi_m$ is the mean of $|\psi|$. Therefore the relative distortion of the wave function is characterized by the integral $\int_0^\infty Vr\,dr$.†

Let us now separate the angular variables in (2.8). To do this, we shall expand $\exp(ik\boldsymbol{v}.\boldsymbol{r})$ and $\psi$ into partial waves:

$$e^{ik\boldsymbol{v}.\boldsymbol{r}} = \sum_{l=0}^{\infty}[4\pi(2l+1)]^{\frac{1}{2}}i^l\frac{u_l(kr)}{r}Y_{l0}(\theta) \tag{2.17}$$

where $\theta$ is the angle between $\boldsymbol{v}$ and $\boldsymbol{r}$ and

$$u_l = \left(\frac{\pi r}{2k}\right)^{\frac{1}{2}} J_{l+\frac{1}{2}}(kr) \tag{2.18}$$

$$\psi = \sum_l [4\pi(2l+1)]^{\frac{1}{2}}i^l\frac{f_l(k,r)}{r}Y_{l0}(\theta) \tag{2.19}$$

By analogy with spectroscopic notation the functions $f_0(k,r)$, $f_1(k,r)$, $f_2(k,r)\ldots$ are referred to respectively as the $s, p, d\ldots$ waves. It will also be convenient to expand the Green's function $G_0$ defined by (2.7) in the form

$$G_0(\boldsymbol{r},\boldsymbol{r}') = \sum_{l,\mu} 2\frac{\Gamma_l(r,r')}{rr'}Y_{l\mu}(\theta,\varphi)\,Y_{l\mu}(\theta'\varphi') \tag{2.20}$$

$Y_{l_\mu}$ are the normalized spherical harmonics, $\Gamma_l$ is the one-dimensional Green's function

$$\Gamma_l(r,r') = \begin{cases} -u_l(kr)v_l(kr') & r \leqslant r' \\ -v_l(kr)u_l(kr') & r' \leqslant r \end{cases} \tag{2.21}$$

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† This estimate is adequate only if $\psi$ does not change too rapidly over the range of $r$ in which $V$ is appreciable.

where $u_l$ is given by (2.18) and $v_l$ is defined by

$$v_l = \frac{1}{i}\left(\frac{\pi kr}{2}\right)^{\frac{1}{2}} H^{(1)}_{l+\frac{1}{2}}(kr) \tag{2.22}$$

Substituting these expansions into (2.8) we obtain the integral equation for $f_l(r)$:

$$f_l(r) = u_l(r)+2v_l(r)\int\limits_0^r u_l(r')V(r')f_l(r')\,dr' + 2u_l\int\limits_r^\infty v_l(r')V(r')f_l(r')\,dr' \tag{2.23}$$

The asymptotic form of $f_l$ when $r \to \infty$ is

$$f_l(r) \sim \frac{1}{k}\sin\left(kr - \frac{l\pi}{2}\right) + q_l e^{i\left(kr-\frac{l\pi}{2}\right)} \tag{2.24}$$

where $q_l$ is the partial scattering amplitude given by

$$q_l = -2\int\limits_0^\infty u_l(r)V(r)f_l(r)dr \tag{2.25}$$

The amplitude $q$ can be expressed as a sum of the partial amplitudes if we substitute the above expansions into (2.10):

$$q = \sum_l [4\pi(2l+1)]^{\frac{1}{2}} q_l Y_{l,0}(\theta) \tag{2.26}$$

The total cross-section $\sigma$ can also be expressed as a sum of the partial cross-sections $\sigma_l$:

$$\sigma = \sum \sigma_l \tag{2.27}$$

$$\sigma_l = 4\pi(2l+1)|q_l|^2 \tag{2.28}$$

The optical theorem can be used to establish the relation between the imaginary part and the modulus of $q_l$. Substituting (2.26) into (2.13) we have

$$|q_l|^2 = \frac{1}{k}\operatorname{Im} q_l \tag{2.29}$$

Since the amplitude $q_l$ may be written in the form

$$q_l = |q_l|\, e^{i\delta_l} \tag{2.30}$$

there follows

$$q_l = e^{i\delta_l}\frac{1}{k}\sin\delta_l = \frac{1}{2ik}(e^{2i\delta_l}-1) \tag{2.31}$$

or

$$q_l = \frac{1}{k\cot\delta_l - ik} \tag{2.32}$$

We can now use (2.31) to transform the asymptotic expression given by (2.24) so that it includes the phase $\delta_l$. After some rearrangement we find:

$$f_l \sim \frac{e^{i\delta_l}}{k}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right) \tag{2.33}$$

It is clear that the relationships given by (2.30) and (2.33) define the phase only to within a multiple of $\pi$. This limitation can be removed by means of the natural condition

$$\lim_{E\to\infty} \delta_l = 0 \tag{2.34}$$

The partial cross-section $\sigma_l$ is given in terms of $\delta_l$ by

$$\sigma_l = 4\pi \frac{2l+1}{k^2} \sin^2 \delta_l \tag{2.35}$$

It is evident from this formula that

$$\sigma_l \leqslant (2l+1)\frac{4\pi}{k^2} \tag{2.36}$$

The function $f_l$ is the solution of the differential equation

$$\frac{d^2 f_l}{dr^2} + \left(k^2 - \frac{l(l+1)}{r^2} - 2V\right) f_l = 0 \tag{2.37}$$

where

$$f_l(0) = 0 \tag{2.38}$$

The function $f_l(r)$ has the required asymptotic behaviour at large $r$. In addition, let us consider the functions which have the given behaviour for small $r$. We shall denote them by $x_l(r)$. In some respects they have advantages over $f_l(r)$. Since both functions are solutions of the same differential equation (2.37) and both vanish when $r = 0$, their ratio must be independent of $r$ and is a function of $k$ only. We may therefore make the substitution:

$$x_l(k, r) = L_l(k) f_l(k, r) \tag{2.39}$$

and require that the functions $x_l$ should behave as $u_l(kr)$ for small $r$. Substituting (2.39) into (2.33) we have, after some rearrangement

$$x_l(r) = u_l(r) + \int_0^r [v_l(r) u_l(r') - u_l(r) v_l(r')] 2V(r') x_l(r')\, dr' \tag{2.40}$$

$$L_l(k) = 1 - 2\int_0^\infty v_l V x_l\, dr \tag{2.41}$$

We note that the function $v_l$ has a pole of the form $r^{-l}$ at $r = 0$. Moreover $V$ has a Coulomb singularity at $r = 0$. It follows that $v_l V$ has a pole of the form $r^{-l-1}$ or $r^{-l}$. However, since $f_l$ falls off as $r^{l+1}$ when $r \to 0$, it follows that the integrands in (2.40) and (2.41) remain finite at the lower limit. The function $L_l$ defined by (2.41) is identical with the so-called Jost function [6]. In view of the connection between the Bessel and Hankel functions, we have

$$v_l = k[(-1)^{l+1} u_{-l-1} - i u_l] \tag{2.42}$$

We can use this relation to rewrite (2.40) and (2.41) in the form

$$x_l = u_l + (-1)^{l+1} k \int_0^r [u_{l-1}(r) u_l(r') - u_l(r) u_{-l-1}(r')] 2V(r') x_l(r')\, dr' \tag{2.43}$$

$$L = 1 + (-1)^l k \int_0^\infty u_{-l-1} 2V x_l\, dr + ik \int_0^\infty u_l 2V x_l\, dr \tag{2.44}$$

It follows from the properties of Bessel functions that at given $r$ the expressions $u_l k^{-l}$ and $u_{-l-1} k^{l+1}$ are analytic functions of $k^2$. Therefore $k^{-l} x$ is an analytic function of $k^2$ at fixed $r$. Hence, $L_l$ may be written in the form

$$L_l = A_l(k) + ik^{2l+1} B_l(k) \tag{2.45}$$

where $A_l$ and $B_l$ are even functions of a real $k$, defined by

$$\begin{aligned} A_l &= 1 + (-1)^l k \int_0^\infty u_{-l-1} 2V x_l\, dr \\ B_l &= k^{-2l} \int_0^\infty u_l 2V x_l\, dr \end{aligned} \tag{2.46}$$

The partial scattering amplitude $q_l$ can be expressed in terms of $L_l$. Using (2.39) and (2.46) we can rewrite (2.25) in the form

$$q_l = -\frac{k^{2l} B_l(k)}{L_l} \tag{2.47}$$

Let

$$L_l = |L_l|\, e^{i\varphi_l} \tag{2.48}$$

The quantity $\varphi_l$ is found to be closely related to the phase $\delta_l$ introduced above. This can be shown by substituting (2.48) into (2.47) and utilizing (2.45):

$$q_l = -\frac{1}{k} e^{-i\varphi_l} \sin \varphi_l \tag{2.49}$$

Comparison of (2.49) with (2.31) then shows that $\varphi_l = -\delta_l + 2\pi N$. The term $2\pi N$ is unimportant and can be removed by a suitable choice of origin of $\varphi_l$. We shall therefore set

$$\varphi_l = -\delta_l \tag{2.50}$$

The properties of $L_l$ when $k$ is complex are of interest. They can be conveniently investigated with the aid of (2.41). By using the asymptotic expressions for $u_l$ and $v_l$ and the expression for $x_l$ given by (2.40) we can verify that $L_l$ is analytic at least over the upper half-plane. Its properties in the lower half-plane depend on the behaviour of $V(r)$ as $r \to \infty$. If $V$ falls off as a power of $r$, that is $V \sim r^{-n}$, then in the lower $k$ half-plane $L$ is not analytic. If, on the other hand, $V \sim e^{-\alpha r}/r$, as is often the case, then $L_l$ is analytic in the lower half-plane within the band $|\mathrm{Im}\, k| < \frac{1}{2}\alpha$.

If the potential energy $V$ is negative, then the existence of bound states with energies $-|E_1|, -|E_2| \ldots$ is, in general, possible. Negative energies correspond to imaginary wave numbers $k_i = i\kappa_i = i\sqrt{2|E_i|}$. It may be shown that the function $L_l(k)$ vanishes at the points $i\kappa_1, i\kappa_2, \ldots$. Let us substitute $k = i\kappa$ into (2.40) and require that $x_l(i\kappa, r)$ vanishes when $r \to \infty$, as in a bound state. In view of the asymptotic behaviour of the Bessel functions of complex arguments, we find that as $r \to \infty$ the coefficient of $u_l(r)$ must vanish, which in turn implies that $L_l = 0$. It may be shown that all these roots are simple ones.

When $V(r)$ behaves at infinity as a Coulomb potential, as for example in the case of the scattering of an electron by an ion, the above equations must be modified in view of the particular asymptotic properties of the wave functions for the continuous spectrum of the Coulomb field. To make this modification, let

$$V(r) = W(r) - \frac{Z}{r} \tag{2.51}$$

considering the attractive interaction in which we shall be interested later. We introduce the Green's function $G_C$ for the Coulomb field:

$$\left(\tfrac{1}{2}\Delta + \tfrac{1}{2}k^2 + \frac{Z}{r}\right) G_C = -\delta(\mathbf{r} - \mathbf{r}') \tag{2.52}$$

Instead of (2.3), we now have

$$\psi = \psi_C - \int G_C W \psi \, d\mathbf{r}' \tag{2.53}$$

where the function $\psi_C$ is the wave function for the continuous spectrum of the Coulomb field whose asymptotic behaviour for $r \to \infty$ is

$$\psi_C \sim e^{i[k\mathbf{v}.\mathbf{r} + \gamma \ln (k\mathbf{v}.\mathbf{r} - kr)]} + q_C \frac{1}{r} e^{ikr + \gamma \ln 2kr} \tag{2.54}$$

where

$$\gamma = \frac{Z}{k} \tag{2.55}$$

and $q_C$ is the scattering amplitude in the Coulomb field and is given by

$$q_C = \frac{\gamma}{2k} \frac{\Gamma(1 + i\gamma)}{\Gamma(1 - i\gamma)} \frac{1}{\sin^2 \frac{\theta}{2}} e^{i\gamma \ln 2 \sin^2 \frac{\theta}{2}} \tag{2.56}$$

The problem is to find the solution of (2.53) which has the asymptotic form given by (2.54) but with an amplitude corresponding to the potential energy (2.51). In order to separate the angular variables, let

$$\psi_C = \sum_l [4\pi(2l+1)]^{\frac{1}{2}} i^l \frac{u_l^C(r)}{r} Y_{l0}(\theta) \tag{2.57}$$

where $u_l^C$ is the regular solution of

$$\frac{d^2u_l^C}{dr^2}+\left(k^2-\frac{l(l+1)}{r^2}+\frac{2Z}{r}\right)u_l^C=0 \tag{2.58}$$

which, when $r\to\infty$, has the asymptotic form

$$u_l^C\sim\frac{1}{k}\sin\left(kr-\frac{l\pi}{2}+\gamma\ln 2kr\right)+q_{C,l}\,e^{i\left(kr-\frac{l\pi}{2}+\gamma\ln 2kr\right)} \tag{2.59}$$

where $q_{C,l}$ is the partial scattering amplitude in the Coulomb field:

$$q_{C,l}=\frac{\Gamma(l+1+i\gamma)}{\Gamma(l+1-i\gamma)} \tag{2.60}$$

We shall take the Green's function $G_C$ in the form

$$G_C(\mathbf{r},\mathbf{r}')=\sum_{l,\mu}2\frac{\Gamma_l(r,r')}{rr'}\,Y_{l\mu}(\theta,\varphi)\,Y_{l\mu}(\theta'\varphi') \tag{2.61}$$

where

$$\Gamma_l(r,r')=\begin{cases}-u_l^C(r)v_l^C(r') & r\leqslant r'\\ -v_l^C(r)u_l^C(r') & r\geqslant r'\end{cases} \tag{2.62}$$

where $u_l^C$ is defined by (2.58) and (2.59), and $v_l^C$ is a non-regular solution of (2.58) whose asymptotic form is

$$v_l\sim-e^{i\left(kr-\frac{l\pi}{2}+\gamma\ln 2kr\right)} \tag{2.63}$$

We write the function $\psi$ in the form of a series analogous to (2.57):

$$\psi=\sum_l\,[4\pi(2l+1)]^{\frac{1}{2}}\,i^l\frac{f_l(r)}{r}\,Y_{l0}(\theta) \tag{2.64}$$

For the functions $f_l$ we obtain

$$f_l(r)=u_l^C(r)+2\int_0^r v_l^C(r)u_l^C(r')W(r')f_l(r')\,dr'+2\int_r^\infty u_l^C(r)v_l^C(r')W(r')f_l(r')\,dr' \tag{2.65}$$

For large $r$ we have

$$f_l(r)\sim\frac{1}{k}\sin\left(kr-\frac{l\pi}{2}+\gamma\ln 2kr\right)+(q_{C,l}+\tilde{q}_l)\,e^{i\left(kr-\frac{l\pi}{2}+\gamma\ln 2kr\right)} \tag{2.66}$$

where

$$\tilde{q}_l=-2\int_0^\infty u_l^C(r)W(r)f_l(r)\,dr \tag{2.67}$$

It follows that the partial scattering amplitude $q_l$ in the field (2.51) is given by

$$q_l=q_{C,l}+\tilde{q}_l \tag{2.68}$$

If we now let

$$q_l = \frac{1}{2ik}(e^{2i\delta_l}-1), \qquad q_{c,l} = \frac{1}{2ik}(e^{2i\eta_l}-1) \tag{2.69}$$

and

$$\delta_l = \eta_l + \mu_l \tag{2.70}$$

we obtain

$$\tilde{q}_l = \frac{1}{2ik}\, e^{2i\eta_l}(e^{2i\mu_l}-1) \tag{2.71}$$

When $r \to \infty$ we have, using (2.66) and (2.69),

$$f_l \sim \frac{1}{k}\, e^{2i\delta_l} \sin\left(kr - \frac{l\pi}{2} + \gamma \ln 2kr + \delta_l\right) \tag{2.72}$$

The integral equation (2.65) will now be transformed to a form analogous to equations (2.40) and (2.41). To accomplish this, equation (2.65) will be rewritten in the form

$$f_l(r) = u_l^C(r)\left[1 + 2\int_0^\infty v_l^C(r') f_l(r') W(r')\, dr'\right] +$$

$$+ 2\int_0^r [v_l^C(r) u_l^C(r') - v_l^C(r') u_l^C(r)]\, W(r') f_l(r')\, dr' \tag{2.73}$$

If we substitute

$$y_l(k, r) = L_l^C(k) f_l(k, r)$$

we obtain

$$y_l(r) = u_l^C(r) + 2\int_0^\infty [v_l^C(r) u_l^C(r') - v_l^C(r') u_l^C(r)]\, W(r') y_l(r')\, dr' \tag{2.74}$$

$$L_l^C(k) = 1 - 2\int_0^\infty v_l^C W y_l\, dr' \tag{2.75}$$

Consequently,

$$\tilde{q}_l = \frac{-2\int_0^\infty u_l^C W y_l\, dr}{1 - 2\int_0^\infty v_l^C W y_l\, dr} \tag{2.76}$$

## 3. SCATTERING AMPLITUDE AND PHASE

It is evident from equations (2.47) and (2.50) that the properties of the amplitude $q_l$ and phase $\delta_l$ are determined by the quantity $L_l$. Using equations (2.48) and (2.45) we can express cot $\delta_l$ in terms of $A_l$ and $B_l$:

$$k^{2l+1} \cot \delta_l = -\frac{A_l(k)}{B_l(k)} \tag{3.1}$$

Hence it follows that cot $\delta_l$ is an odd function of $k$. Since $\delta(\pm\infty) = 0$ we find that the phase $\delta_l$ is itself an odd function of $k$, i.e.

$$\delta_l(k) = -\delta_l(-k) \tag{3.2}$$

On this definition $\delta_l$ will in general experience a discontinuity at $k = 0$. Since $L_l$ vanishes on the imaginary axis at points corresponding to bound states, we can establish with the aid of (3.2) an important relationship between the number $N_l$ of levels with given $l$ and the quantity $\delta_l(+0)$, i.e. the limit of $\delta_l(k)$ for $k \to 0$ on the side of positive $k$. This relationship is

$$\delta_l(+0) = N_l\pi \tag{3.3}$$

and is known in the literature as Levinson's theorem. In order to prove this result we recall that, according to Cauchy's theorem, the change in phase of $L_l(k)$ for integration over the contour shown in Fig. 3, i.e. the quantity $-[\delta(-0)-\delta(+0)]/2\pi$, is equal to the number of zeros of $L_l(k)$ within the domain enclosed by this contour in the plane of complex $k$. All the zeros of $L_l$ lie along the imaginary axis and their number if $N_l$. Consequently,

$$-[\delta(-0)-\delta(+0)] = 2\pi N_l \tag{3.4}$$

If we now combine equations (3.2) and (3.4) we obtain the result given by (3.3).

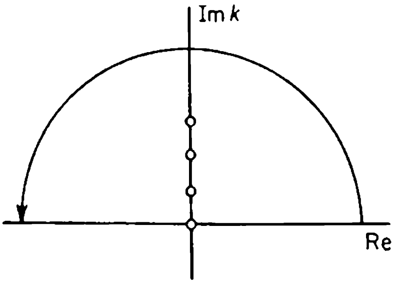

FIG. 3. Levinson's theorem. The points on the imaginary axis are the zeros of the function $L$

A special case arises when $L_l(0) = 0$. This situation occurs, for example, when one of the discrete energy levels merges with the boundary of the continuous spectrum, i.e. tends to zero as the depth of the potential well is reduced. Under these conditions $L_l(0) = 0$ and the phase is given by

$$\delta_l(+0) = N\pi + \frac{\pi}{2} \tag{3.5}$$

where $N$ is the number of levels (not including the special level with zero energy).

Let us consider the limiting value of $q_l$ as $k \to 0$. We shall start with the expression given by equation (2.47). Substituting equation (2.45) into (2.47) we obtain

$$q_l = \left(ik - \frac{A_l(k)}{k^{2l}B_l(k)}\right)^{-1} \tag{3.6}$$

Suppose that $A_l(0) \neq 0$ (when $A_l(0) = 0$, it follows from equation (2.49) that $L_l(0) = 0$, i.e. we have the special case mentioned above). It follows that

$$\begin{aligned} &\lim_{k\to 0} q_l = 0 \qquad \text{when } l \neq 0 \\ &\lim_{k\to 0} q_0 = -\frac{B_0(0)}{A_0(0)} \end{aligned} \tag{3.7}$$

i.e. all the partial amplitudes except the zero-order amplitude vanish and the amplitude of the $s$-wave is, in general, the only one to have a non-zero value. The limiting value of this amplitude is usually denoted by $-a$, where $a$ is the scattering length. Thus,

$$a = \frac{B_0(0)}{A_0(0)} \tag{3.8}$$

According to equation (3.1) we have

$$\lim_{k\to 0} k \cot \delta_0 = -\frac{1}{a} \tag{3.9}$$

We can use the latter relation to show that the scattering length is equal, apart from the sign, to the derivative of the phase angle $\delta$ with respect to the wave number $k$, i.e.

$$a = -\left(\frac{d\delta}{dk}\right)_{k=0} \tag{3.10}$$

If there is an $s$-level with zero energy, then the amplitude $q_0(k)$ increases without limit as $1/k$ when $k \to 0$ (resonance scattering). Under these conditions, equation (3.10) is no longer valid. If there is a $p$-level with zero energy, then

$$\lim_{k\to 0} \frac{A_1(k)}{k^2 B_1(k)}$$

is finite and therefore

$$\lim_{k\to 0} q_1 \neq 0$$

The partial amplitude for $l = 1$ has a non-zero value when $k = 0$. Partial amplitudes for $l > 1$ vanish independently of whether a zero level with given $l$ exists or not.

Let us consider in greater detail the sign and magnitude of the scattering length. From the definition given by equation (3.8) and the expressions in (2.46) we have

$$a = \frac{2\int_0^\infty V x_0 r \, dr}{1 + 2\int_0^\infty V x_0 \, dr} \tag{3.11}$$

In a repulsive field $V > 0$. For zero energy, the function $x_0$ satisfies the equation

$$x_0 = r+2\int_0^r (r-s)Vx_0\,ds$$

and is therefore everywhere positive. It follows that the scattering length $a$ is positive. In an attractive field $V < 0$, and if there are bound states the function $x_0$ has no nodes (apart from the origin) and is everywhere positive. Therefore the integral in the numerator of (3.11) is negative. The denominator remains positive as $V$ passes from positive values through zero to negative values. The denominator in equation (3.11), which is equal to $A_0(0)$, vanishes (and the scattering length becomes infinite) only when a bound state with zero energy appears. In an attractive field the scattering length is negative in the absence of a bound state. In the presence of bound states, the scattering length can be either positive or negative, since the sign and magnitude of the integrals in equation (3.11) depend on the number and position of the nodes of the function $x_0$. All the possible cases can be conveniently illustrated by introducing a parameter $\alpha$, which characterizes the intensity of the field of force, and considering the dependence of $a$ on $\alpha$.

Let

$$V(r) = \alpha V_0(r) \tag{3.12}$$

and assume that $V_0 > 0$. On this definition a positive $\alpha$ corresponds to repulsion and a negative $\alpha$ to attraction.

On the basis of the general properties of functions satisfying Volterra's integral equations, we can state that for given $k$ and $r$ the function $x_0$ will be an analytic function of $\alpha$. It follows that $a$ will be a meromorphic function of $\alpha$.

Figure 4 shows the general character of the dependence of $a$ on $\alpha$. The

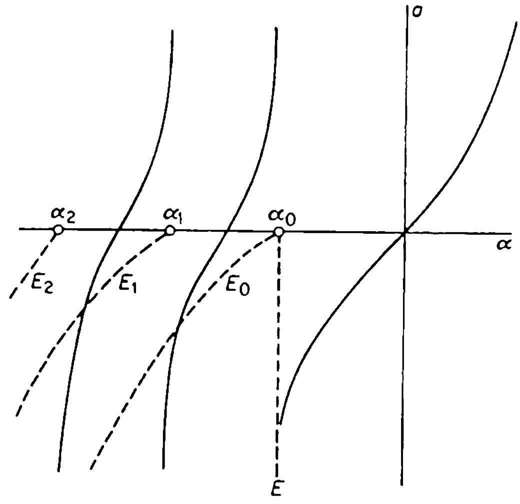

FIG. 4. Dependence of the scattering length and the energy levels $E_0$, $E_1$, ... (broken curves) on the parameter $\alpha$

points $\alpha_0, \alpha_1, \ldots$ are the values at which the first, second, ..., levels with zero energy appear as the depth of the potential well increases. The broken curves represent the dependence of the energy of the first, second, and so on, levels on the depth of the potential well. As can be seen from Fig. 4, the scattering length, and with it the scattering cross-section at zero energy, become equal to zero (Ramsauer effect) for certain values of the parameter $\alpha$. As an example, consider the dependence of the scattering length of an electron in a Thomas-Fermi field due to a nuclear charge $Z$ [7] (see Fig. 5). Figure 5 is a mirror image of Fig. 4, since $-Z$ plays the role of $\alpha$.

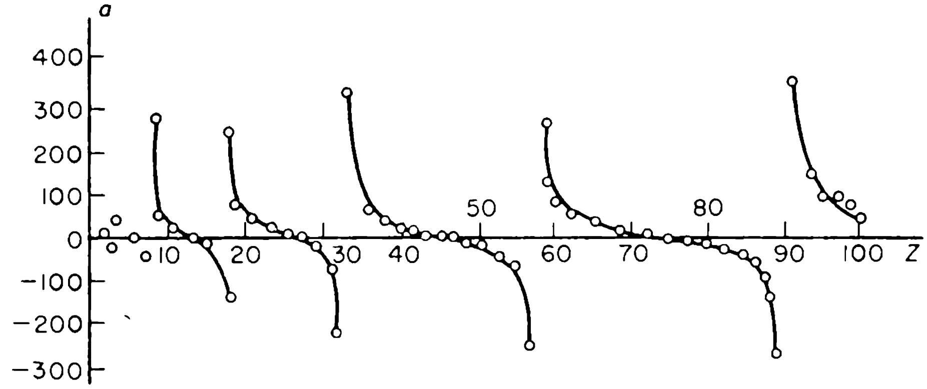

FIG. 5. Dependence of the scattering length for electrons (in units of 0·885/$Z$) on the nuclear charge $Z$ in the Thomas-Fermi field

Let us now consider the behaviour of the amplitude $q_l$ as a function of $k$ for small $k$. If the potential energy falls off as $r \to \infty$ more rapidly than any negative power of $r$, then $L_l$ will be an analytic function not only in the upper half-plane of complex $k$ but also in a band in the lower half-plane. Consequently, $A_l$ and $B_l$ can be expanded into a series in powers of $k$ (within the limits of convergence), and in view of the fact that $A_l$ and $B_l$ are even, these will in fact be power series in $k^2$ when $k$ is real. We can then write

$$\frac{A_l(k)}{B_l(k)} = \frac{A_l^{(0)} + k^2 A_l^{(1)} + \ldots}{B_l^{(0)} + k^2 B_l^{(1)} + \ldots} \tag{3.13}$$

If $k$ is so small that $B_l$ vanishes in the interval between 0 and $k$, we can expand $1/(B_l^{(0)} + k^2 B_l^{(1)} + \ldots)$ in powers of $k^2$, giving

$$\frac{A_l(k)}{B_l(k)} = \frac{A_l^{(0)}}{B_l^{(0)}} + k^2 \left[\frac{A_l^{(1)}}{B_l^{(0)}} - \frac{A_l^{(0)} B_l^{(1)}}{B_l^{(0)2}}\right] + \ldots \tag{3.14}$$

Let

$$\frac{A_l^{(0)}}{B_l^{(0)}} = \frac{1}{a_l}; \qquad \frac{A_l^{(1)}}{B_l^{(0)}} - \frac{A_l^{(0)} B_l^{(1)}}{B_l^{(0)2}} = -\tfrac{1}{2} r_l \tag{3.15}$$

so that equation (3.14) may be rewritten in the form

$$\frac{A_l}{B_l} = \frac{1}{a_l} - \tfrac{1}{2} r_l k^2 + \ldots \tag{3.16}$$

On substituting the latter series into equation (3.1) we have

$$k^{2l+1} \cot \delta_l = -\frac{1}{a_l} + \tfrac{1}{2} k^2 r_l + \ldots \tag{3.17}$$

We can now use equation (2.32) to obtain the following expression for $q_l$:

$$q_l = \frac{k^{2l}}{-\frac{1}{a_l} + \frac{1}{2} k^2 r_l + i k^{2l+1}} \tag{3.18}$$

In the special case $l = 0$, the expansion given by (3.17) becomes identical with the well-known formula [8]

$$k \cot \delta_0 = -\frac{1}{a_0} + \tfrac{1}{2} k^2 r_0 \tag{3.19}$$

originally obtained by a different method. The quantity $r_0$ in this expression is called the effective range of the forces.

If for given $l$ there exists an energy level such that $\kappa_l \ll 1$, it is possible to obtain a relation between $a_l$, $r_l$ and $\kappa_l$ by using equation (3.16) and assuming that $k = i\kappa$. Since $L_l(i\kappa) = 0$, it follows from equation (2.45) that

$$\frac{A_l(i\kappa)}{B_l(i\kappa)} = (-1)^{l+1} \kappa^{2l+1} \tag{3.20}$$

Therefore we have

$$(-1)^l \kappa^{2l+1} = \frac{1}{a_l} + \tfrac{1}{2} \kappa^2 r_l \tag{3.21}$$

and in particular when $l = 0$

$$\frac{1}{a_0} = \kappa (1 + \tfrac{1}{2} \kappa r_0) \tag{3.22}$$

If the potential energy falls off as $r^{-n}$ when $r \to \infty$, then $L_l$ is not analytic in the lower half-plane of complex $k$, and therefore $A_l$ and $B_l$ cannot be expanded in powers of $k$. It follows that the expressions given by equations (3.19) and (3.22) will no longer hold.

As an example, consider the energy of interaction between a point charge and an induced dipole which at large distances is of the form

$$V \sim -\frac{\beta}{r^4} \tag{3.23}$$

This expression is encountered, for example, in the case of scattering of an electron by an atom when polarization of the atom by the incident electron is taken into account. In this case, (3.19) is replaced by [9]

$$k\cot\delta_0 = -\frac{1}{\alpha} + \frac{\pi\beta}{3\alpha^2}|k| + \frac{4\beta}{3\alpha}k^2\ln\left(\frac{\beta|k|}{4}\right) + \ldots \tag{3.24}$$

When $l \neq 0$ we have instead of equation (3.17)

$$k^2\cot\delta_l = \frac{8(l+\frac{3}{2})(l+\frac{1}{2})(l-\frac{1}{2})}{\pi\beta} + \ldots \tag{3.25}$$

Therefore as $k \to 0$ the amplitude $q_l$ falls off as $k$ for all $l$.

Let us also consider the behaviour of the amplitude as $k \to 0$ when the field is of the Coulomb type. According to equation (2.68) the analysis can be reduced to the investigation of $\tilde{q}_l$, since the scattering amplitude $q_{lC}$ in the Coulomb field is known. We shall confine our attention to the case $l = 0$.

The dependence of $\tilde{q}$ on $k$ can be analysed with the aid of equation (2.76). However, it will be useful to express the functions $v_l^C$ and $u_l^C$ (with given asymptotic behaviour) in terms of a function having a given behaviour at the origin. Let $x_r$ and $x_i$ be two linearly independent solutions of the equation

$$\frac{d^2x_{i,r}}{dr^2} + \left(k^2 + \frac{2Z}{r}\right)x_{i,r} = 0 \tag{3.26}$$

where

$$\begin{aligned} x_r &\to r \\ x_i &\to 1 \end{aligned} \tag{3.27}$$

when $r \to 0$. We then have

$$u^C = e^{i\eta}C_0x_r(r) \tag{3.28}$$

$$v^C = e^{-i\eta}\left(\frac{1}{C_0}x_i + ikC_0x_r\right) \tag{3.29}$$

where

$$C_0 = \left(\frac{2\pi Z/k}{1-e^{-2\pi Z/k}}\right)^{\frac{1}{2}} \tag{3.30}$$

When $k \ll 2\pi Z$, the quantity $C_0$ is approximately equal to $(2\pi Z/k)^{\frac{1}{2}}$. It follows from equations (3.28) and (3.27) that as $k \to \infty$ the function $u^C$ increases as $k^{-\frac{1}{2}}$. According to equation (2.74), the function $u_l(r)$ should also increase as $k^{-\frac{1}{2}}$ when $r \to 0$. It is evident from equation (3.25) that $v^C$ falls off as $k^{\frac{1}{2}}$ as $k \to 0$, so that the product $v^Cy_l$ remains finite as $r \to 0$. The quantity $\tilde{q}_l$ increases as $1/k$ when $k \to 0$ (this is evident from equation (2.76)).

So far, we have discussed the general properties of the phase $\delta$ and amplitude $q$ without considering their numerical values. Let us now proceed to the calculation of the phase $\delta$. In principle, this requires the solution of equation (2.37). However, this equation has an analytical solution only for a certain special form of $V$. In all other cases it can be solved only numerically. Equation (2.37) is inconvenient for the evaluation of the phase, since the function $f_l$ is oscillatory and does not tend to any definite limit as $r \to \infty$.

However, it is possible to reduce the problem to the integration of a first-order non-linear equation for the function $\eta_l(r)$, whose limit as $r \to \infty$ is equal to the phase $\delta_l$ [10], and which exhibits monotonic variation for monotonic $V$.

Consider the logarithmic derivative

$$\varphi = \frac{1}{f_l}\frac{df_l}{dr} \tag{3.31}$$

It satisfies

$$\frac{d\varphi}{dr} + \varphi^2 = 2V + \frac{l(l+1)}{r^2} - k^2 \tag{3.32}$$

and may be written in the form

$$\varphi = \frac{\dfrac{du_l}{dr}\cos\eta_l(r) + (-1)^l \dfrac{du_{-l-1}}{dr}\sin\eta_l(r)}{u_l\cos\eta_l(r) + (-1)^l u_{-l-1}\sin\eta_l(r)} \tag{3.33}$$

If we substitute equation (3.33) into (3.32) and bear in mind the equations satisfied by $u_l$ and $u_{-l-1}$, and the fact that

$$u_l\frac{du_{-l-1}}{dr} - u_{-l-1}\frac{du_l}{dr} = (-1)^{l+1}k \tag{3.34}$$

we obtain

$$\frac{d\eta_l}{dr} = -\frac{2V}{k}[u_l\cos\eta_l(r) + (-1)^l u_{-l-1}\sin\eta_l(r)]^2 \tag{3.35}$$

For large $r$ the function $\eta_l(r)$ in equation (3.33) may be replaced by $\eta_l(\infty)$, so that by using the asymptotic form of the Bessel functions we have

$$\varphi \sim \frac{d}{dr}\ln\left[\sin\left(kr - \frac{l\pi}{2}\right)\cos\eta_l(\infty) + \right.$$
$$\left. + \cos\left(kr - \frac{l\pi}{2}\right)\sin\eta_l(\infty)\right] = \frac{d}{dr}\ln\sin\left[kr - \frac{l\pi}{2} + \eta_l(\infty)\right] \tag{3.36}$$

On substituting equations (3.36) and (3.31) we find that the asymptotic expression for $f_l$ which corresponds to equation (3.36) is

$$f_l(r) \sim \text{const}\sin\left[kr - \frac{l\pi}{2} + \eta_l(\infty)\right] \tag{3.37}$$

from which it follows that

$$\eta_l(\infty) = \delta_l \tag{3.38}$$

Consider the behaviour of $\eta_l(r)$ for $r \to 0$.

Since $f_l \sim r^{l+1}$ for small $r$, we have

$$\lim_{r\to 0} \varphi r = l+1 \tag{3.39}$$

On the other hand, it follows from equation (3.33) that for small $r$

$$\varphi r = (l+1)\frac{1-l(l+1)\eta_l(r)(kr)^{-2l-1}}{1+\eta_l(r)(kr)^{-2l-1}} \tag{3.40}$$

Hence in view of equation (3.39) we obtain

$$\lim_{r\to 0} \eta_l(r)(kr)^{-2l-1} = 0 \tag{3.41}$$

i.e. numerical integration of equation (3.35) should be carried out subject to the condition $\eta_l(0) = 0$ for all $l$.

## 4. Dispersion Relations

Consider the matrix element $T(E, \nu, E, \nu')$. According to equations (1.21) and (1.16)

$$T(E,\nu,E,\nu') = \int \varphi_0^* V \varphi_0\, d\mathbf{r} - \lim_{\varepsilon\to +0} \int \varphi_0^* V \hat{G}(E+i\varepsilon) V \varphi_0\, d\mathbf{r} \tag{4.1}$$

If we recall the explicit form of the function $\varphi_0$ given by equation (1.3) and replace the resolvent $\hat{G}$ by the Green's function $G(\mathbf{r}, \mathbf{r}', E+i0)$, we have in the case of forward scattering ($\nu = \nu'$)

$$T(E,\nu,E,\nu) = \frac{k}{(2\pi)^3}\int V\, d\mathbf{r} - \frac{k}{(2\pi)^3}\frac{1}{4\pi}\int e^{ik\nu.(\mathbf{r}-\mathbf{r}')} V(\mathbf{r}) G(\mathbf{r},\mathbf{r}') V(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' \tag{4.2}$$

If we multiply the latter expression by $-(2\pi)^2/k$ and let $-\int V\, d\mathbf{r} = 2\pi q_0$, we have in view of equation (2.11)

$$q - q_0 = \frac{1}{8\pi^2}\int e^{ik\nu.(\mathbf{r}-\mathbf{r}')} V(\mathbf{r}) G(\mathbf{r},\mathbf{r}') V(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' \tag{4.3}$$

Let

$$q - q_0 = F \tag{4.4}$$

and consider the analytical properties of $F$ in the plane of complex energy $z = E+i\varepsilon$ cut along the positive real axis; this corresponds to the upper half-plane of complex $k$. The properties of $F$ are determined by the properties of the Green's function $G(\mathbf{r}, \mathbf{r}', z)$. For a sufficiently rapid decrease in $V(r)$ at large distances (faster than $r^{-3}$), the function $G$ has the following properties in the $z$-plane [11]:

1. $G(\mathbf{r}, \mathbf{r}'\, z)$ is analytic in the $z$-plane with a cut along the positive real axis and has, in general, simple poles on the negative real axis $E = -|E_j|$. These poles correspond to discrete energy eigenvalues in the field $V$. Using the eigenfunction expansion of $G$

$$G(\mathbf{r},\mathbf{r}',z) = \sum_j \frac{\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')}{z-E_j} \tag{4.5}$$

or in the presence of degeneracy,

$$G(\mathbf{r}, \mathbf{r}', z) = \sum_{j,\lambda} \frac{\psi_{j\lambda}(\mathbf{r})\psi^*_{j\lambda}(\mathbf{r}')}{Z - E_j} \tag{4.6}$$

we see that the residues at the poles $z = E_j$ are equal to

$$\sum_{\lambda} \psi_{j\lambda}(\mathbf{r})\psi^*_{j\lambda}(\mathbf{r}')$$

2. The limit $\lim\limits_{\varepsilon \to +0} G(\mathbf{r}, \mathbf{r}', E + i\varepsilon)$ exists for all $E > 0$.
3. $$G(\mathbf{r}, \mathbf{r}', E + i0) = G^*(\mathbf{r}, \mathbf{r}', E - i0) \tag{4.7}$$
4. For large $|z|$

$$|G - G_0| \leqslant C_E e^{-|\mathbf{r}-\mathbf{r}'|\operatorname{Im} k}$$

where $G_0$ is the Green's function for free motion (2.7); $C_E \to 0$ when $E \to \infty$.

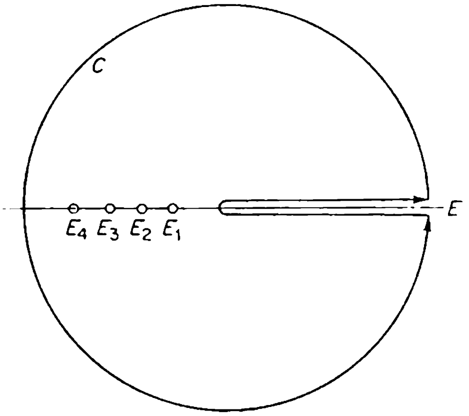

FIG. 6. Derivation of the dispersion formula. $E_1, E_2, \ldots$ represent the bound-state energy levels

It follows from these properties that the integral on the right-hand side of equation (4.2) converges absolutely for all $z$ and is an analytic function of $z$ everywhere on the cut plane except for the poles of the Green's function $G$; moreover,

$$F(E + i0) = F^*(E - i0) \tag{4.8}$$

$$\lim_{|z| \to \infty} F(z) = 0 \tag{4.9}$$

We now derive the dispersion relation [11, 12]. Consider the contour $C$ in the $z$-plane (Fig. 6). From Cauchy's theorem

$$F(z) = \frac{1}{2\pi i} \int_C \frac{F(z')\,dz'}{z' - z} - \sum_j \frac{d_j}{|E_j| + z} \tag{4.10}$$

where

$$d_j = \frac{1}{8\pi^2} \sum_\lambda \int e^{\varkappa_j \mathbf{r}\cdot\boldsymbol{\nu}} V\psi_\lambda \, d\mathbf{r} \int e^{-\varkappa_j \mathbf{r}'\cdot\boldsymbol{\nu}} V\psi_{j\lambda} \, d\mathbf{r}' \tag{4.11}$$

are the residues of $F$ at the poles $z' = -|E_j|$ (we recall that $d_j$ are real). As the radius of the circle tends to infinity, the contribution due to the integrand on the circle tends to zero in view of equation (4.9). There remains only the integral along the boundary of the cut:

$$F(z) = \frac{1}{2\pi i} \int_0^\infty \frac{F(E'+i0)}{E'-z} dE' - \frac{1}{2\pi i} \int_0^\infty \frac{F(E'-i0)}{E'-z} dE' - \sum_j \frac{d_j}{|E_j|+z} \tag{4.12}$$

From equation (4.8) we have

$$F(z) = \frac{1}{\pi} \int_0^\infty \frac{\operatorname{Im} F(E')}{E'-z} dE' - \sum_j \frac{d_j}{|E_j|+z} \tag{4.13}$$

Now let $\operatorname{Im} z \to 0$ so that $z \to E$. Since

$$\lim_{\varepsilon \to 0} \frac{1}{E'-E-i\varepsilon} = \mathscr{P} \frac{1}{E'-E} + i\pi\delta(E'-E) \tag{4.14}$$

where $\mathscr{P}$ represents the principal part, we have

$$\operatorname{Re} F(E) = \frac{1}{\pi} \mathscr{P} \int_0^\infty \frac{\operatorname{Im} F(E')}{E'-E} dE' - \sum_j \frac{d_j}{|E_j|+E} \tag{4.15}$$

Since $2\pi q_0 = -\int V \, d\mathbf{r}$ is real, the expression given by equation (4.15) may be written in the form

$$\operatorname{Re} q = q_0 + \frac{1}{\pi} \mathscr{P} \int_0^\infty \frac{\operatorname{Im} q(E') \, dE'}{E'-E} - \sum_j \frac{d_j}{|E_j|+E} \tag{4.16}$$

We can now use the optical theorem (2.13) to express $\operatorname{Im} q$ in terms of the scattering cross-section:

$$\operatorname{Im} q = \frac{k}{4\pi} \sigma$$

so that

$$\operatorname{Re} q(E) = q_0 + \frac{1}{4\pi^2} \mathscr{P} \int_0^\infty \frac{\sigma(E') k' \, dE'}{E'-E} - \sum_j \frac{d_j}{|E_j|+E} \tag{4.17}$$

It is interesting to consider the limiting case of equation (4.17) when $E = 0$. Since the amplitude $q$ at zero energy is related to the scattering length by

$q(0) = -a$, it follows from equation (4.17) that when $E = 0$:

$$a = a_0 - \frac{1}{2\pi^2}\int_0^\infty \sigma\, dk + \sum_j \frac{d_j}{|E_j|} \tag{4.18}$$

The importance of the dispersion relations in collision theory lies in that they can be used to derive rigorous formulae for quantities directly related to measured values, and can therefore serve as a criterion for the analysis of experimental data (see § 16).

*Chapter 2*

# APPROXIMATE METHODS FOR THE DETERMINATION OF WAVE FUNCTIONS AND SCATTERING AMPLITUDES

## 5. Perturbation Theory

In § 2 we estimated the effect of the field of force on the wave function near the centre of force for $k = 0$, and saw that it could be characterized by the quantity $\int\limits_0^\infty Vr\, dr$.

If $\int\limits_0^\infty |V|r\, dr \ll 1$, this effect is small for $k = 0$ and even more so when $k \neq 0$, so that $V$ can be regarded as a small perturbation. Let $V = \alpha V_0$ as in equation (3.12) and expand the solution of (2.8) into the series

$$\psi = \sum \alpha^n \psi^{(n)} \tag{5.1}$$

Let us take a plane wave for $\psi^{(0)}$

$$\psi^{(0)} = e^{ik\nu . r} \tag{5.2}$$

The expression for $\psi^{(n)}$ is then

$$\psi^{(n)} = -\frac{1}{2\pi}\int \frac{e^{ik|r-r'|}}{|r-r'|} V_0 \psi^{(n-1)}(r')\, dr' \tag{5.3}$$

The scattering amplitude $q$ will also be expanded into a power series:

$$q = \sum q^{(n)} \alpha^{n+1} \tag{5.4}$$

It follows from equation (2.10) that

$$q^{(n)} = -\frac{1}{2\pi}\int e^{-ik\nu . r}\, V_0 \psi^{(n)}\, dr' \tag{5.5}$$

The first term in the expansion (5.4), namely

$$q^{(0)} = -\frac{1}{2\pi}\int V_0\, e^{-ik(\nu-\nu').r'}\, dr' \tag{5.6}$$

represents the well-known Born approximation. If $V_0$ is independent of the angles, we can carry out integration with respect to the angles in equation (5.6). The result is

$$q^{(0)} = -2\int\limits_0^\infty V_0 \frac{\sin Kr}{Kr} r^2\, dr \tag{5.7}$$

The quantity

$$K = 2k\sin\frac{\theta}{2} \tag{5.8}$$

is the momentum (in atomic units) transferred to the centre of force as a result of scattering through an angle $\theta$, where $\theta$ is the angle between $\boldsymbol{\nu}$ and $\boldsymbol{\nu}'$. From the formula

$$\frac{\sin Kr}{Kr} = \sum_l [4\pi(2l+1)]^{\frac{1}{2}} Y_{l,0}(\theta)\frac{u_l^2(kr)}{r^2} \tag{5.9}$$

and using equation (2.26), we obtain the following expression for the partial amplitude on the Born approximation:

$$q_l^{(0)} = -2\int_0^\infty V_0 u_l^2\,dr \tag{5.10}$$

It is evident from the expression for $q_l$ given by equation (2.47), and from equations (2.45) and (2.46), that the partial amplitude $q_l$ is a meromorphic function of the interaction constant $\alpha$. Consequently, the expansion given by (5.4) (and the equivalent expansion for the partial amplitudes) is only valid for values of $\alpha$ smaller than the radius of convergence (a detailed investigation of the convergence of the series for $q$ in powers of $\alpha$ is given in [13]).

However, the expression for the partial amplitude can be written in the form of a ratio of two series of powers of $\alpha$ [14], which is valid for all $\alpha$. With this purpose in mind, let

$$x_l = \sum_0^\infty \alpha^n x_l^{(n)} \tag{5.11}$$

in (2.40) and assume that

$$x_l^{(0)} = u_l \tag{5.12}$$

Then,

$$x_l^{(n)} = 2k(-1)^{l+1}\int_0^r [u_{-l-1}(r)u_l(r') - u_{-l-1}(r')u_l(r)]x_l^{(n-1)}V_0\,dr' \tag{5.13}$$

It follows from the general properties of Volterra's integral equations that the series given by (5.11) converges for all $\alpha$.

If we substitute equation (5.11) into (2.44), we obtain the following series for the Jost function

$$L_l = \sum a^n L_l^{(n)} \tag{5.14}$$

where

$$L_l^{(0)} = 1 \tag{5.15}$$

$$L_l^{(1)} = 2(-1)^l k\int_0^\infty V_0 u_l u_{-l-1}\,dr + 2ik\int_0^\infty V_0 u_l^2\,dr \tag{5.16}$$

$$L_l^{(n)} = 2(-1)^l k\int_0^\infty u_l x_l^{(n)} u_{-l-1}\,dr + 2ik\int_0^\infty V_0 u_l x_l^{(n)}\,dr \tag{5.17}$$

Finally, substituting equation (5.14) into (2.47) we obtain

$$q_l = -\frac{1}{k}\frac{\sum \alpha^n \operatorname{Im} L_l^{(n)}}{\sum \alpha^n L_l^{(n)}} \tag{5.18}$$

The approximate expression for $q_l$ can be obtained by cutting off the series in the numerator and denominator. In particular, if we retain first-order terms only, we have, in view of equation (5.15),

$$q_l = -\frac{\alpha}{k}\left(\frac{\operatorname{Im} L_l^{(1)}}{1+\alpha L_l^{(1)}}\right) \tag{5.19}$$

or on substituting the explicit expression given by (5.16)

$$q_l = \frac{-2\int\limits_0^\infty V u_l^2\, dr}{1+2k\int\limits_0^\infty V u_l u_{-l-1}\, dr + 2ik\int\limits_0^\infty V u_l^2\, dr} \tag{5.20}$$

Comparison of (5.20) and (5.10) shows that the Born approximation can be obtained from (5.20) if the integrals in the denominator are neglected in comparison with unity.

As an example of the application of Born's approximation consider the scattering of a charged particle by a distributed charge of density $\rho$ where

$$\int \rho\, d\boldsymbol{r} = Z \tag{5.21}$$

In this case, the amplitude $q^{(0)}$ can be directly expressed in terms of $\rho$. Suppose that $Z_0$ is the charge on the particle. Its potential energy $V$ must then satisfy the equation

$$\Delta V = -4\pi Z_0 \rho \tag{5.22}$$

Moreover, we can write

$$\Delta e^{i\boldsymbol{K}.\boldsymbol{r}} = -K^2 e^{i\boldsymbol{K}.\boldsymbol{r}} \tag{5.23}$$

On multiplying equation (5.22) by $\exp(i\boldsymbol{K}.\boldsymbol{r})$ and (5.23) by $V$, we have on subtracting and integrating over all space

$$\int [e^{i\boldsymbol{K}.\boldsymbol{r}} \Delta V - V\Delta(e^{i\boldsymbol{K}.\boldsymbol{r}})]\, d\boldsymbol{r} = K^2 \int e^{i\boldsymbol{K}.\boldsymbol{r}}\, V\, d\boldsymbol{r} - 4\pi Z_0 \int e^{i\boldsymbol{K}.\boldsymbol{r}} \rho\, d\boldsymbol{r} \tag{5.24}$$

According to Green's theorem, the integral on the left-hand side vanishes if $V$ has no singularities and falls off sufficiently rapidly as $r \to \infty$. If this is so,

$$\int e^{i\boldsymbol{K}.\boldsymbol{r}}\, V d\boldsymbol{r} = -\frac{4\pi}{K^2}\int e^{i\boldsymbol{K}.\boldsymbol{r}} \rho\, d\boldsymbol{r} \tag{5.25}$$

so that

$$q^{(0)} = \frac{2Z_0}{K^2}\int e^{i\boldsymbol{K}.\boldsymbol{r}} \rho\, d\boldsymbol{r} \tag{5.26}$$

The quantity

$$F(K) = \frac{1}{Z}\int e^{iK.r}\rho\, dr \tag{5.27}$$

is known as the form factor. It can be used to rewrite equation (5.26) as:

$$q^{(0)} = \frac{2Z_0 Z}{K^2} F(K) \tag{5.28}$$

If $V(r)$ has a Coulomb singularity, this singularity must be considered separately. For example, when the scattering system is an atom of charge $Z_1$ we have

$$V = \frac{Z_1 Z_0}{r} + W \tag{5.29}$$

where $W$ is finite at $r = 0$. We then have

$$q^{(0)} = \frac{2Z_0}{K^2}[Z_1 + ZF(K)] \tag{5.30}$$

For a neutral atom,

$$Z = -Z_1 \tag{5.31}$$

so that the formula given by equation (5.30) becomes

$$q^{(0)} = \frac{2Z_0 Z_1}{K^2}[F(K) - 1] \tag{5.32}$$

## 6. THE METHOD OF TRIAL POTENTIALS

When the potential energy $V$ cannot be regarded as a small perturbation, one can try to choose an expression for $V_0$ such that there is a reasonably simple solution for scattering in this field, and at the same time $V - V_0$ can be regarded as a small perturbation [15]. If we confine our attention to simple trial expressions for $V_0$ which contain only one or two parameters, we cannot, of course, expect to obtain a good approximation to the exact wave function and the exact amplitude over a wide range of energies and angles $\theta$.

However, the situation is more favourable when $kR \lesssim 1$, where $R$ is the range of the field $V$ and $\psi$ is a slowly varying function of $k$ and $\theta$. Having chosen $V_0$ so as to achieve the best approximation to $\psi$ at zero energy, we can use the same expression for $V_0$ to obtain an adequate approximation in the entire interval $0 \lesssim kR \lesssim 1$.

It is natural to choose $V$ so that there are no effects of the first order in $V - V_0$.

Consider the limiting case of zero energy. The wave functions $\psi$ and $\psi_0$ corresponding to $V$ and $V_0$ respectively satisfy the equations

$$\Delta\psi - 2V\psi = 0 \tag{6.1}$$

$$\Delta\psi_0 - 2V_0\psi_0 = 0 \tag{6.2}$$

and have an asymptotic behaviour of the form

$$\psi = 1 + \frac{q}{r} \tag{6.3}$$

$$\psi_0 = 1 + \frac{q_0}{r} \tag{6.4}$$

Let us multiply equation (6.1) by $\psi_0$, (6.2) by $\psi$ and then subtract and integrate over all space. In view of (6.3) and (6.4) we have

$$2\pi(q - q_0) = \int (V - V_0)\psi_0 \psi \, dr \tag{6.5}$$

We shall require that $q = q_0$, so that from equation (6.5):

$$\int (V - V_0)\psi_0 \psi \, dr = 0 \tag{6.6}$$

On a first approximation we can replace $\psi$ by $\psi_0$, so that

$$\int (V - V_0)\psi_0^2 \, dr = 0 \tag{6.7}$$

which is the condition for first-order effects to vanish in perturbation theory (see, for example, [17] Section 10).

Consider now the condition which must be satisfied by the difference $\delta V = V - V_0$ for it to be looked upon as a small perturbation. Let

$$\delta\psi = \psi - \psi_0 \tag{6.8}$$

The equation for $\delta\psi$ follows from (6.1) and (6.2) and is

$$\Delta\delta\psi - 2V_0\,\delta\psi = 2\delta V\psi \tag{6.9}$$

Furthermore, consider the irregular solution of the equation

$$\Delta\varphi - 2V_0\varphi = 0 \tag{6.10}$$

which behaves as $1/r$ when $r \to 0$. If we multiply equation (6.9) by $\varphi$, (6.10) by $\delta\psi$ and then subtract and integrate over all space, we obtain, taking into account the singularity in $\varphi$ at $r \to 0$,

$$\delta\psi(0) = \frac{1}{2\pi} \int \delta V \varphi \psi \, dr \tag{6.11}$$

The order of magnitude will be retained if $\varphi$ is replaced by $1/r$ in the integrand. Hence,

$$|\delta\psi(0)| \lesssim (\max|\psi|) 2 \int_0^\infty |\delta V| r \, dr \tag{6.12}$$

The quantity $|\delta\psi(0)|/\max|\psi|$ may be looked upon as a measure of the relative departure of $\psi$ from $\psi_0$ within the sphere of action of the field of force. It is evident from (6.12) that the condition for this departure to be small is

$$2 \int_0^\infty |\delta V| r \, dr \ll 1 \tag{6.13}$$

When $V_0 = 0$ this condition becomes identical with the condition for the applicability of perturbation theory for $V$ (§ 5), as should be the case.

If the trial expression for $V_0$ contains one parameter, equation (6.7) can be used to define it. If equation (6.13) is then not satisfied, it is necessary to introduce additional parameters in order to reduce the magnitude of $\int\limits_0^\infty |\delta V| r\, dr$. An example illustrating the possibilities of this method will be considered in § 13.

## 7. The Variational Method

The problem involving the scattering of a particle by a centre of force may be formulated as a variational problem involving the determination of the stationary value or an extremum of a functional. This formulation is used to establish certain general relationships such as, for example, the virial theorem [16], and also in the development of the variational method for approximate calculations.

In the variational method one chooses a suitable analytical expression for the continuous-spectrum wave function, i.e. the so-called trial function which contains a number of parameters. The parameters are determined by requiring that the functional which includes the wave function should exhibit either an extremum or a stationary value.

Apart from the latter condition, there are a number of integral relations which the wave function must satisfy. The exact function satisfies all the conditions whereas the trial function may satisfy only a few of them. The various modifications of the variational method differ from each other by the number of integral relations satisfied by the trial function.

In this discussion we shall confine our attention to Kohn's method and the interesting consequences recently established on this method in the case of zero energy.

Consider the functional

$$\mathscr{L} = \int \varphi^*(\nu_2, r)(H-E)\psi(\nu_1, r)\, dr \tag{7.1}$$

where $\psi$ and $\varphi$ have the asymptotic forms

$$\psi \sim e^{ik\nu . r} + q\frac{e^{ikr}}{r} \tag{7.2}$$

$$\varphi \sim e^{ik\nu . r} + q'\frac{e^{-ikr}}{r} \tag{7.3}$$

and $q$ and $q'$ are not necessarily the exact amplitudes. The functional vanishes for functions $\psi$ which are exact solutions of the equation

$$(H-E)\psi = 0 \tag{7.4}$$

We shall vary the functions $\psi$, $\varphi$ so that in the asymptotic expression $q$, $q'$ change by $\delta q$ and $\delta q'$ respectively. The details of the calculations are given in [17]. We shall not reproduce them here but merely state the final result:

$$\delta\mathscr{L} = 2\pi\,\delta q(\nu_1,\nu_2) \tag{7.5}$$

It follows that the expression

$$Q = -\frac{1}{2\pi}\mathscr{L}+q \tag{7.6}$$

is stationary with respect to variations in the wave function, and that its value is equal to the amplitude $q$ when exact wave functions are employed. Suppose now that instead of the exact wave function $\psi$ we use a trial function $\psi_t$ containing a few adjustable parameters and having the asymptotic form

$$\psi_t \sim e^{ik\mathbf{v}.\mathbf{r}}+q_t\frac{e^{ikr}}{r} \tag{7.7}$$

Let the value of the functional (7.1) calculated with the aid of this function be denoted by $\mathscr{L}_t$.

The approximate expression for the scattering amplitude in Kohn's method is taken to be the stationary value of (7.6) obtained using the function $\psi_t$, i.e.

$$q_K = \mathrm{st}\left(-\frac{1}{2\pi}\mathscr{L}_t+q_t\right) \tag{7.8}$$

In particular, if $\psi_t$ includes the parameters $c_1, c_2, \ldots, c_n$, the conditions that $\mathscr{L}_t$ should be stationary with respect to $c_1, c_2, \ldots, c_n, q_t$ are [in view of (7.5)]

$$\frac{\partial\mathscr{L}_t}{\partial c_i} = 0 \tag{7.9}$$

$$\frac{\partial\mathscr{L}_t}{\partial q_t} = 2\pi \tag{7.10}$$

In the above discussion, we have only used the fact that the functional $Q$ is stationary. The problem as to whether (7.8) yields the upper or lower bounds remains unresolved. In order to determine the nature of the approximation which can be achieved by the variational method, consider [18] the phase of the $s$-wave. Let $\psi = f(r)/\sqrt{4\pi}\,r$. The function $f(r)$ will be normalized so that it has the asymptotic form

$$f \sim \frac{1}{k}\sin kr+\lambda\cos kr \tag{7.11}$$

in order to avoid complex quantities. If $\psi$ is the exact wave function, $\lambda = (\tan\delta)/k$. If, on the other hand, $\psi$ is the trial function, then according to Kohn

$$\frac{1}{k}\tan\delta = \lambda-2\int_0^\infty f(H-E)f\,dr \tag{7.12}$$

where we must take the stationary value of the functional.

Let us take the trial function in the form

$$f = \varphi + \sum_{i=1}^{m} c_i \chi_i \tag{7.13}$$

where

$$\varphi = \frac{1}{k} \sin kr + \lambda \varphi_0(r) \cos kr \tag{7.14}$$

and $\varphi_0(r)$ is a function which vanishes at $r = 0$ and is equal to unity when $r \to \infty$, but is arbitrary in all other respects; $\chi_i$ are functions which fall off rapidly as $r \to \infty$ and $c_i$ are the constants to be varied. We then have

$$\frac{1}{k} \tan \delta = \lambda + \sum_{i,j} c_i c_j M_{ij} + 2 \sum_i c_i R_i + B \tag{7.15}$$

where

$$M_{ij} = M_{ji} = 2 \int_0^\infty \chi_i (E-H) \chi_j \, dr \tag{7.16}$$

$$R_i = 2 \int_0^\infty \chi_i (E-H) \varphi \, dr \tag{7.17}$$

$$B = 2 \int_0^\infty \varphi (E-H) \varphi \, dr \tag{7.18}$$

Variation of the constants $c_i$ yields

$$\sum_{j=1}^{N} M_{ij} c_j = -R_i \tag{7.19}$$

or in matrix form

$$\mathrm{MC} = -\mathrm{R} \tag{7.20}$$

The matrix $\mathrm{M}^{-1}$ may turn out to be singular when a determination is made of $k$ and the other parameters entering into $\chi_i$. The solution given by (7.20) will then not exist. Near these values the phase expressed as a function of $k$ undergoes rapid changes and may be either much greater or much smaller than the true value.

Specific calculations in a particular example [18] (see also § 16) show that as the number of terms in equation (7.13) is increased, there is an increase in the number of singularities in $\mathrm{M}^{-1}$, but that the phase fluctuations near these points are gradually smoothed out.

However the limit of zero energy is a special case. It turns out that Kohn's expression for the amplitude [equation (7.8)] gives the upper bound for the scattering length. The case when there is no bound state of the particle in the central force field and the case when the bound state does exist must be considered separately.

Let $\psi_t$ be the trial function at zero energy which, in view of equation (7.7), has the asymptotic form

$$\psi_t \sim 1 - \frac{a_t}{r} \tag{7.21}$$

and consider the difference between $\psi_t$ and the exact function $\psi$:

$$g = \psi_t - \psi \tag{7.22}$$

We shall use the following identity which can be verified directly

$$a = a_t + \frac{1}{2\pi} \int \psi_t H \psi_t \, dr - \frac{1}{2\pi} \int gHg \, dr \tag{7.23}$$

where $a$ is the exact scattering length. The quantity

$$a_K = a_t + \frac{1}{2\pi} \int \psi_t H \psi_t \, dr \tag{7.24}$$

is, according to equation (7.8), the Kohn scattering length if $\psi_t$ is taken to be the function giving the stationary value of $a_K$. Consequently,

$$a = a_K - \frac{1}{2\pi} \int gHg \, dr \tag{7.25}$$

Consider the integral

$$J = \int gHg \, dr \tag{7.26}$$

In the absence of bound states, $H$ is a positive definite operator in the space of square-integrable functions. However, $f$ is not square-integrable. We therefore introduce the integral

$$J(\lambda) = \int g \, e^{-\lambda r} Hg \, e^{-\lambda r} \, dr \tag{7.27}$$

which includes the square-integrable function $g \exp(-\lambda r)$; for $\lambda = 0$ this becomes identical with (7.26). The integral $J(\lambda)$ is such that $J(\lambda) > 0$. We shall show that $J$ remains positive when $\lambda \to 0$. To prove this, it will be sufficient to show that $J(\lambda)$ is continuous at $\lambda = 0$.

Consider the difference

$$J(\lambda) - J(0) = \int g(e^{-2\lambda r} - 1)Hg \, dr + \lambda^2 \int g^2 \, e^{-2\lambda r} \, dr - 2\lambda \int g \nabla g \, e^{-2\lambda r} \, dr \tag{7.28}$$

Since $|g(r)|$ has an upper limit for all $r$ and $\nabla g \to 0$ when $r \to \infty$, it can be shown that each of the three terms on the right-hand side of (7.28) becomes as small as desired when $\lambda \to 0$; this proves the continuity of $J(\lambda)$. Therefore the integral given by (7.26) is positive, or in the limiting case zero. It then follows from (7.25) that

$$a \leqslant a_K \tag{7.29}$$

i.e. the Kohn scattering length is the upper-limit approximation for the scattering length.

Consider now the case when there are bound states. We shall assume for simplicity that there is only one such state. Let

$$H_{ik} = \int \psi_i^* H \psi_k \, dr \qquad i, k = 1, 2 \tag{7.30}$$

be the matrix elements of the energy operator $H$ calculated with the aid of the orthogonal functions $\psi_1$ and $\psi_2$, where $\psi_1$ is an adequate trial function for the single bound state, so that $H_{11} < 0$.

Let us reduce the matrix

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

to the diagonal form

$$\begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

One of the eigenvalues, $E_1$, will be negative and the other, $E_2$, positive or zero, so that

$$E_1 E_2 \leqslant 0 \tag{7.31}$$

Since the product $E_1 E_2$ of the eigenvalues is equal to the determinant of the matrix $\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$ it follows that

$$H_{11} H_{22} - H_{12}^2 \leqslant 0 \tag{7.32}$$

We note that since $\psi_2$ enters twice into each of the terms in the inequality, the normalizing factor of $\psi_2$ is unimportant. The inequality (7.32) remains valid when $\psi_2$ is replaced by another function $\psi_2'$ which is not orthogonal to $\psi_2$. This may be verified by substituting

$$\psi_2 = \psi_2' - \psi_1 \int \psi_2'^* \psi_1 \, dr \tag{7.33}$$

The inequality (7.32) then becomes

$$H_{11} H_{22}' - H_{12}'^2 \leqslant 0 \tag{7.34}$$

where the dashed matrix elements represent the replacement of $\psi_2$ by $\psi_2'$.

If we now take a suitable bound-state function for $\psi_1$ and let

$$\varepsilon_t = -E_t \tag{7.35}$$

where $E_t$ is the value of $H_{11}$ calculated using $\psi_1$; and if we replace $\psi_2$ by $g$, we have instead of (7.34)

$$\int gHg \, dr \leqslant -\frac{1}{\varepsilon_t}\left(\int \psi_1 Hg \, dr\right)^2 \tag{7.36}$$

Since $Hg = H(\psi_t - \psi) = H\psi_t$ (because $H\psi = 0$) we may write

$$-\int gHg \, dr \leqslant \frac{1}{\varepsilon_t}\left(\int \psi_1 H\psi_t \, dr\right)^2 \tag{7.37}$$

Then (7.25) becomes

$$a \leqslant a_K + \frac{1}{2\pi\varepsilon_t}\left(\int \psi_1 H\psi_t \, dr\right)^2 \tag{7.38}$$

Therefore the right-hand side of (7.38) is the upper bound for the scattering length.

It is important to note that (7.38) includes the trial function and the variational energy but it does not include the exact bound-state wave function and the exact value of the binding energy.

The inequality given by (7.38) may be rewritten in the form

$$a \leqslant a'_K \tag{7.39}$$

where $a'_K$ is Kohn's scattering length calculated using the function

$$\psi'_t = \psi_t - \frac{1}{\varepsilon_t}\psi_1 \int \psi_1 H\psi_t \, dr \tag{7.40}$$

The orthogonality condition $\int \psi_1 \psi'_t \, dr = 0$ is satisfied. It is evident from this that in Kohn's method the trial function can reasonably be taken in a form containing the variational function of the bound state in addition to other expressions.

## 8. THE METHOD OF TRIAL FUNCTIONS

In the variational method the optimum parameters of the trial function are determined from the condition that the functional should be an extremum. However there are other methods for determining the optimum values of the trial-function parameters. One method is based on the use of certain relationships which are satisfied by the exact wave function [20, 21]. Depending on which particular relationships are employed in the determination of the parameters, it is possible to modify the method in various ways. In the simplest case the trial function contains only one parameter. According to [20], the parameter may be determined from the integral equation for the scattering amplitude given by equation (2.25). It is convenient to choose the parameter so that it plays the role of the amplitude in the asymptotic expression for the trial function

$$f_l \sim \frac{1}{k}\sin\left(kr - \frac{l\pi}{2}\right) + q_l e^{i\left(kr - \frac{l\pi}{2}\right)} \tag{8.1}$$

The equation for $q_l$ is then of the form

$$q_l = -2\int_0^\infty u_l V f_l \, dr \tag{8.2}$$

If the trial function $F_l$ depends on the $n$ parameters $c_1, c_2, \ldots, c_n$ in addition to $q_l$, and has the asymptotic form

$$f_l \sim \frac{1}{k}\sin\left(kr - \frac{l\pi}{2}\right) + q_l e^{i\left(kr - \frac{l\pi}{2}\right)} \tag{8.3}$$

then one of the possible methods of determining these parameters is as follows. Substitute $f(c_1, c_2, \ldots, c_n, q_l, r)$ into the right-hand side of the integral equation (2.23). This yields the function

$$g_l(c_1, c_2, \ldots, c_n, q_l, r) = u_l(r) + 2\int_0^r [v_l(r)u_l(r') - u_l(r)v_l(r')]V(r')f_l(r')\,dr' \quad (8.4)$$

Since $f_l$ is not an exact solution of (2.23), it follows that $g_l \neq f_l$. We expand $g_l$ and $f_l$ into series in powers of $r$ and require that the first $n$ terms be identical. This yields a system of equations for the coefficients $c_n$. In order to determine the amplitude $q_l$, we substitute $f_l$ into the integral relation for the amplitude (8.2).

The application of one of the variants of the method of trial functions to the scattering of electrons by atoms has been described in a number of papers [21].

The disadvantage of the method of trial functions is the absence of a criterion of the type given by (7.29) which would determine the nature of the approximation in the limiting case of zero energy. Moreover, determination of the coefficients $c_n$ by means of the expansion of the trial function $f_l(r)$ in powers of $r$ becomes ineffective when the potential well is so deep that the wave function has a number of zeros inside the well.

*Chapter 3*

# COLLISIONS OF ELECTRONS WITH HYDROGEN ATOMS: GENERAL THEORY

## 9. Basic Relationships

The collision of an electron with a hydrogen atom is one of the simplest processes, particularly when the energy of the incident electron is insufficient to excite the atom and the scattering is elastic. Nevertheless, even the description of elastic scattering of electrons by hydrogen atoms is theoretically quite a difficult problem.

We now consider the main factors which characterize the scattering of a slow electron by an atom. Suppose for the sake of simplicity that the electron shell of the atom is "frozen" so that it does not exhibit any changes during the interaction. The effect of the atom on an electron can then be determined by considering an equivalent centre of force. The interaction between the electron and the atom is in fact found to be attractive in character.

It sometimes happens that when the atom is regarded as a centre of force there exists a shallow zero energy level for the electron, i.e. a negative ion can be formed, or that there is a virtual level. As a result, low-energy scattering approaches resonance scattering. Even this single fact complicates quantitative discussion of the problem quite considerably (for example, it prevents us from using the perturbation theory).

When the electron shell of the atom is "unfrozen" a new factor arises, namely, polarization of the atom by the scattered electron. At large distances between the electron and the atom the influence of polarization may be described by an interaction of the form $U = -\beta/r^4$, where $\beta$ is the polarizability of the atom. This expression represents the interaction between the point charge and the induced dipole. However, at small distances, a single coefficient $\beta$ is insufficient to describe the polarization effect. In contrast to the static polarization of an atom in a homogeneous field, we must now deal with the more complicated dynamic polarization. Moreover, the indistinguishability of the electrons has a major effect on the various detailed features of the scattering process. As a result, the so-called exchange-scattering, in which the incident electron changes places with the atomic electrons, becomes indistinguishable from simple scattering and both must be regarded as a single process. Mathematically, the indistinguishability of the electrons is reflected in the symmetry properties of the wave function. When these symmetry properties are taken into account, it is found that the effective interaction between the electron and the atom becomes non-local, and the equations for the wave function $F(r)$ of the scattered electron include an exchange operator of the form

$$\hat{W}F = \int W(r', r)F(r')\,dr'$$

in addition to the central-force term $VF$.

When excitation is possible the theory becomes even more complicated. In elastic scattering calculations it is necessary to solve only one equation when polarization is neglected. When excitation is possible the corresponding calculation (on the same approximation) requires the solution of at least two equations even when there is only one inelastic scattering channel. When there are several channels it is necessary to consider a complicated set of equations, since the cross-sections for processes in the different channels are related, in view of the conservation of the number of particles, which is expressed mathematically by the unitary property. It follows that the elastic scattering is also modified under the influence of inelastic scattering.

The effect of all these factors on the collision between an electron and atom, their relative importance, and the connection between them, have not as yet been adequately explored, although it is possible to write down the equations which formally represent the exact theory including all the above factors.

We now consider the theory of time-dependent states, which is analogous to the theory in § 1.† The energy operator is of the form

$$H = H_0(r_1)+H_0(r_2)+V_0(r_1)+V_0(r_2)+V(r_1, r_2) \tag{9.1}$$

where $H_0(r_1)$ and $H_0(r_2)$ are kinetic energy operators for the first and second electrons respectively, $V_0(r_1)$ and $V_0(r_2)$ are the energies of interaction between the electrons and the nucleus, and $V(r_1, r_2)$ is the energy of interaction between the electrons:

$$V_0(r_1) = -\frac{1}{r_1}, \qquad V_0(r_2) = -\frac{1}{r_2}, \qquad V(r_1, r_2) = \frac{1}{|r_1 - r_2|} \tag{9.2}$$

The wave function for the electron + atom system depends on the coordinates and the spin variables of the electrons. In the non-relativistic theory the total spin of the system is a constant of motion, so that we can separate out the spin variables and confine our attention to the coordinate part of the wave function. Since the total wave function is antisymmetric with respect to the interchange of coordinates and spins, there is a connection between the symmetry properties of the coordinate part of the wave function and the magnitude of the total spin of the system.

In the case of the two-electron system which we are considering here, there are two possible spin states, namely, a triplet and a singlet state. In the triplet state the coordinate function is antisymmetric while in the singlet state it is symmetric.

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† The ensuing analysis is a variant of the so-called theory of rearrangement collisions for two particles in the field of a fixed centre of force. It will be assumed that the two particles do not form a bound state. The various problems in the theory of rearrangement collisions are discussed in [22–25].

Let $\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, t)$ be the coordinate part of the wave function satisfying the equation

$$i\frac{\partial\Phi}{\partial t} = H\Phi$$

As has been pointed out above, the function $\Phi$ should be symmetric or antisymmetric with respect to the interchange of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. However, it is in many ways more convenient to begin without assigning symmetry properties to $\Phi$ and to symmetrize the result in the final stages of the analysis.

Proceeding as in § 1, we shall express $\Phi$ on the interaction representation, that is, we expand $\Phi$ in terms of the eigenfunctions for a non-interacting electron-atom system. Two such systems can be formed. One is described by the operator

$$H_1 = H_0(\boldsymbol{r}_1) + V_0(\boldsymbol{r}_1) + H_0(\boldsymbol{r}_2) \tag{9.3}$$

and the eigenfunction

$$\varphi_\alpha^{(1)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = k^{\frac{1}{2}}(2\pi)^{-\frac{3}{2}}\, e^{ik\boldsymbol{v}.\boldsymbol{r}_2}\,\psi_\alpha(\boldsymbol{r}_1) \tag{9.4}$$

where $\psi_\alpha$ is the atomic function. The subscript $\alpha$ represents the set of quantum numbers which characterize the state of the atomic electron, i.e. the energy $E_\alpha$, the angular momentum, and the component of the angular momentum in a special direction (in the present case, the direction of motion of the incident electron). The plane wave $\exp(ik\boldsymbol{v}.\boldsymbol{r}_2)$ describes the free motion of the electron with energy $E = \frac{1}{2}k^2$ in the direction of $\boldsymbol{v}$. The functions $\varphi_\alpha^{(1)}$ are normalized to $\delta(E-E')\delta(\boldsymbol{v}-\boldsymbol{v}')\delta_{\alpha\alpha'}$ and satisfy the equation

$$H_1\varphi_\alpha^{(1)} = \mathscr{E}\varphi_\alpha^{(1)} \tag{9.5}$$

where

$$\mathscr{E} = \tfrac{1}{2}k^2 + E_\alpha \tag{9.6}$$

The eigenvalues $\mathscr{E}$ of the operator $H_1$ form the continuous spectrum beginning with the negative quantity $-|E_0|$, which is equal to the ground-state energy of the hydrogen atom.

The other system is described by the operator

$$H_2 = H_0(\boldsymbol{r}_1) + H_0(\boldsymbol{r}_2) + V_0(\boldsymbol{r}_2) \tag{9.7}$$

and the eigenfunction

$$\varphi_\alpha^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = k^{\frac{1}{2}}(2\pi)^{-\frac{3}{2}}\, e^{ik\boldsymbol{v}.\boldsymbol{r}_1}\,\psi_\alpha(\boldsymbol{r}_2) \tag{9.8}$$

whose significance is analogous to equation (9.4), except that $\boldsymbol{r}_1$ has been replaced by $\boldsymbol{r}_2$. Either the functions given by (9.4) or those given by (9.8) can be used as the basic functions. Accordingly, we shall consider the following two equivalent expansions for $\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, t)$:

$$\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = \sum_\alpha \int \Psi_\alpha^{(1)}(\mathscr{E}, \boldsymbol{v}, t)\, e^{-i\mathscr{E}t}\, \varphi_\alpha^{(1)}(\boldsymbol{r}_1, \boldsymbol{r}_2)\, d\mathscr{E}\, d\Omega \tag{9.9}$$

$$\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = \sum_\alpha \int \Psi_\alpha^{(2)}(\mathscr{E}, \boldsymbol{v}, t)\, e^{-i\mathscr{E}t}\, \varphi_\alpha^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)\, d\mathscr{E}\, d\Omega \tag{9.10}$$

As in § 1, we shall assume the existence of the limits

$$\Psi^{(i)}_{\pm\alpha} = \lim_{t\to\pm\infty} \Psi^{(i)}_{\alpha}(\mathscr{E}, \mathbf{v}, t) \qquad i = 1,2 \tag{9.11}$$

and determine the $S$-matrix from the relation

$$\Psi^{(i)}_{+\alpha}(\mathscr{E}, \mathbf{v}) = \sum_{i'\alpha'} \int S^{ii'}(\mathscr{E}, \mathbf{v}, \alpha, \mathscr{E}', \mathbf{v}', \alpha')\Psi^{(i')}_{-\alpha'}(\mathscr{E}', \mathbf{v}')\, d\mathscr{E}'\, d\Omega' \quad i, i' = 1,2 \tag{9.12}$$

Let us express $\Phi$ in the Heisenberg representation. Let $\varphi(\mathbf{r}_1, \mathbf{r}_2, \mathscr{E}, \mathbf{v})$ be the eigenfunction of the operator $H$ corresponding to the eigenvalue $\mathscr{E}$, so that

$$H\varphi = \mathscr{E}\varphi \tag{9.13}$$

where $\mathbf{v}$ is a unit vector which enters into the argument of $\varphi$ (as in § 1). The eigenvalues $\mathscr{E}$ of the operator $H$ form a continuous spectrum lying in the same region as the continuous spectrum of $H_1$ and $H_2$, that is, $-|E_0| \leqslant \mathscr{E} \leqslant \infty$. Moreover, the region $\mathscr{E} < -|E_0|$ includes a discrete level of the negative hydrogen ion, but this level is of no significance in the present context.

In order to determine the function $\varphi$, we must also specify its asymptotic behaviour. We shall suppose that an electron of energy $\frac{1}{2}k_0^2$ is incident on an atom in the state $\alpha_0$, the position vectors of the incident and atomic electrons being respectively $\mathbf{r}_1$ and $\mathbf{r}_2$. Accordingly, the function $\varphi$ will asymptotically tend to $\varphi^{(1)}_{\alpha_0}(\mathbf{r}_1, \mathbf{r}_2)$ as $r_2 \to \infty$. Therefore the function $\varphi$ depends on the parameters defining the initial state of the atom, and this will be implied in the ensuing analysis.

Let us write $\Phi$ in the form

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, t) = \int e^{-i\mathscr{E}t}\,\Psi(E, \mathbf{v})\,\varphi(\mathbf{r}_1, \mathbf{r}_2, \mathscr{E}, \mathbf{v})\, d\mathscr{E}\, d\Omega \tag{9.14}$$

The relation between $\Psi^{(i)}_{\alpha}$ and $\Psi$ can be established by comparing equation (9.14) with (9.9) or (9.10), and is given by

$$\Psi^{(i)}_{\alpha}(\mathscr{E}, \mathbf{v}, t) = \int e^{-i(\mathscr{E}'-\mathscr{E})t}\, w^{(i)}_{\alpha}(\mathscr{E}, \mathbf{v}, \mathscr{E}', \mathbf{v}')\,\Psi(\mathscr{E}', \mathbf{v}')\, d\mathscr{E}'\, d\Omega' \tag{9.15}$$

where

$$w^{(i)}_{\alpha}(\mathscr{E}, \mathbf{v}, \mathscr{E}', \mathbf{v}') = \int \varphi^{(i)*}_{\alpha}(\mathbf{r}_1, \mathbf{r}_2, \mathscr{E}, \mathbf{v})\,\varphi(\mathbf{r}_1, \mathbf{r}_2, \mathscr{E}', \mathbf{v}')\, d\mathbf{r}_1\, d\mathbf{r}_2 \qquad i = 1,2 \tag{9.16}$$

Let us transform equation (9.16) by substituting

$$\varphi(\mathbf{r}_1, \mathbf{r}_2, \mathscr{E}', \mathbf{v}) = \varphi^{(1)}_{\alpha_0} + \chi \tag{9.17}$$

where, in accordance with (9.6),

$$\mathscr{E}' = \tfrac{1}{2}k_0^2 + E_{\alpha_0}$$

We first consider the case $i = 1$. Since

$$(H - \mathscr{E}')\varphi = 0 \tag{9.18}$$

and

$$(H_1 - \mathscr{E}')\varphi^{(1)}_{\alpha_0} = 0 \tag{9.19}$$

we obtain

$$(H-\mathscr{E}')\chi = -(H-H_1)\varphi^{(1)}_{\alpha_0} \tag{9.20}$$

or using the explicit form of $H$ and $H_1$

$$(H-\mathscr{E}')\chi = -[V_0(r_2)+V(\boldsymbol{r}_1,\boldsymbol{r}_2)]\varphi^{(1)}_{\alpha_0} \tag{9.21}$$

By analogy with the method used in § 1, let us define the resolvents

$$\hat{G} = (H-\mathscr{E})^{-1}, \qquad \hat{G}_i = (H_i-\mathscr{E})^{-1}, \qquad i = 1,2,\dots$$

as the limits

$$\begin{aligned} \hat{G}(\mathscr{E}+i0) &= \lim_{\varepsilon\to+0}(H-\mathscr{E}-i\varepsilon)^{-1} \\ \hat{G}_i(\mathscr{E}+i0) &= \lim_{\varepsilon\to+0}(H_i-\mathscr{E}-i\varepsilon)^{-1} \end{aligned} \tag{9.22}$$

With the aid of equation (9.22) we have from (9.21)

$$\chi = -\lim_{\varepsilon\to+0}\hat{G}(\mathscr{E}'+i\varepsilon)[V_0(r_2)+V(\boldsymbol{r}_1,\boldsymbol{r}_2)]\varphi^{(1)}_{\alpha_0} \tag{9.23}$$

On substituting this into (9.17),

$$\varphi = \varphi^{(1)}_{\alpha_0} - \lim_{\varepsilon\to+0}\hat{G}(\mathscr{E}'+i\varepsilon)[V_0(r_2)+V(\boldsymbol{r}_1,\boldsymbol{r}_2)]\varphi^{(1)}_{\alpha_0} \tag{9.24}$$

Again, following the method of Chapter 1, the latter relation may be written in the form

$$\varphi = -\lim_{\varepsilon\to+0}i\varepsilon\hat{G}(\mathscr{E}'+i\varepsilon)\varphi^{(1)}_{\alpha_0} \tag{9.25}$$

The equation for the resolvent

$$\hat{G} = \hat{G}_1 - \hat{G}_1[V_0(r_2)+V(\boldsymbol{r}_1,\boldsymbol{r}_2)]\hat{G} \tag{9.26}$$

can now be used to transform (9.24) so that it reads

$$\varphi = \varphi^{(1)}_{\alpha_0} - \frac{1}{H_1-\mathscr{E}'-i0}[V_0(r_2)+V(\boldsymbol{r}_1,\boldsymbol{r}_2)]\varphi \tag{9.27}$$

This result can be used to reduce the expression for $w^{(1)}_{\alpha}$ to the form

$$w^{(1)}_{\alpha}(\mathscr{E},\boldsymbol{\nu},\mathscr{E}',\boldsymbol{\nu}_0) = \delta(\mathscr{E}-\mathscr{E}')\,\delta(\boldsymbol{\nu}-\boldsymbol{\nu}_0)\,\delta_{\alpha\alpha_0} - \frac{T^{(1)}_{\alpha_0\alpha}(\mathscr{E},\boldsymbol{\nu},\mathscr{E}',\boldsymbol{\nu}_0)}{\mathscr{E}-\mathscr{E}'} \tag{9.28}$$

where

$$\begin{aligned} &T^{(1)}_{\alpha_0\alpha}(\mathscr{E},\boldsymbol{\nu},\mathscr{E}',\boldsymbol{\nu}_0) \\ &\quad= \int \varphi^{*(1)}_{\alpha}(\boldsymbol{r}_1,\boldsymbol{r}_2,\mathscr{E},\boldsymbol{\nu})[V_0(r_2)+V(\boldsymbol{r}_1,\boldsymbol{r}_2)]\,\varphi(\boldsymbol{r}_1,\boldsymbol{r}_2,\mathscr{E}',\boldsymbol{\nu}_0)\,d\boldsymbol{r}_1\,d\boldsymbol{r}_2 \end{aligned} \tag{9.29}$$

Substituting equation (9.28) into (9.15) and repeating the steps analogous to those given in § 1 we obtain

$$\begin{aligned} \Psi^{(1)}_{-\alpha}(\mathscr{E},\boldsymbol{\nu}) &= \Psi(\mathscr{E},\boldsymbol{\nu})\delta_{\alpha\alpha_0} \\ \Psi^{(1)}_{+\alpha}(\mathscr{E},\boldsymbol{\nu}) &= \Psi^{(1)}_{-\alpha}(\mathscr{E},\boldsymbol{\nu}) - 2\pi i\int T^{(1)}_{\alpha_0\alpha}(\mathscr{E},\boldsymbol{\nu},\mathscr{E},\boldsymbol{\nu}_0)\,\Psi^{(1)}_{-\alpha}(\mathscr{E},\boldsymbol{\nu}_0)\,d\Omega' \end{aligned} \tag{9.30}$$

The $S$-matrix element is therefore given by

$$S^{1,1}(\mathscr{E},\boldsymbol{\nu},\alpha,\mathscr{E}',\boldsymbol{\nu}_0,\alpha_0) = \delta(\mathscr{E}'-\mathscr{E})[\delta(\boldsymbol{\nu}_0'-\boldsymbol{\nu})\,\delta_{\alpha\alpha_0} - 2\pi i T^{(1)}_{\alpha_0\alpha}(\mathscr{E},\boldsymbol{\nu},\mathscr{E},\boldsymbol{\nu}_0)] \tag{9.31}$$

The presence of the factor $\delta(\mathscr{E}'-\mathscr{E})$ in (9.31) ensures the conservation of energy ($\mathscr{E} = \mathscr{E}'$). In accordance with equation (9.6), the energy of the final state is $\mathscr{E} = \frac{1}{2}k_\alpha^2+E_\alpha$, and therefore

$$\tfrac{1}{2}k_\alpha^2+E_\alpha = \tfrac{1}{2}k_0^2+E_{\alpha_0} \tag{9.32}$$

Consider now the case $i = 2$ and suppose that the function $\varphi$ is, as before, defined by equation (9.24). The vector $\Psi'^{(2)}_\alpha$ describes the so-called exchange scattering. It is now convenient to express the resolvent $\hat{G}$ in (9.25) in terms of the resolvent $\hat{G}_2$ as in (9.26) rather than in terms of $\hat{G}_1$:

$$\hat{G} = \hat{G}_2-\hat{G}_2[V_0(r_1)+V(r_1,r_2)]\hat{G} \tag{9.33}$$

Substituting (9.33) into (9.25) we obtain

$$\varphi = -\lim_{\varepsilon\to+0} i\varepsilon\hat{G}_2\varphi^{(1)}_{\alpha_0} - \lim_{\varepsilon\to+0}\hat{G}_2[V_0(r_1)+V(r_1,r_2)]\varphi \tag{9.34}$$

We shall show that

$$\lim_{\varepsilon\to0}\varepsilon\hat{G}_2(\mathscr{E}+i\varepsilon)\varphi^{(1)}_{\alpha_0} = 0 \tag{9.35}$$

To do this let us expand $\varphi^{(1)}_{\alpha_0}(r_1, r_2)$ in terms of $\varphi^{(2)}_\alpha$:

$$\varphi^{(1)}_{\alpha_0} = \sum_\alpha \int a_\alpha(\mathscr{E}')\varphi^{(2)}_\alpha\,d\mathscr{E}'\,d\Omega' \tag{9.36}$$

If the atomic function $\psi_\alpha(r_2)$ entering into $\varphi^{(2)}_\alpha$ refers to the discrete spectrum, then $a_\alpha(\mathscr{E}')$ is a continuous function of $\mathscr{E}'$. But if the atomic function $\Psi_\alpha(r_2)$ refers to the continuous spectrum, then the coefficient $a_\alpha(\mathscr{E}')$ has a $\delta$-function type of singularity. However for this part of the spectrum the symbol $\sum_\alpha$ represents integration over the continuous spectrum with respect to $\alpha$, which removes the singularity and leads to a finite expression. Let us operate with $\hat{G}_2(\mathscr{E}+i\varepsilon) = (H_2-\mathscr{E}-i\varepsilon)^{-1}$ on both sides of equation (9.36). The result is

$$\hat{G}_2\varphi^{(1)}_{\alpha_0} = \sum_\alpha \int a_\alpha(\mathscr{E}')\frac{1}{\mathscr{E}-\mathscr{E}'-i\varepsilon}\varphi^{(2)}_\alpha\,d\mathscr{E}'\,d\Omega'$$

The integral

$$J = \int\frac{d\mathscr{E}'}{\mathscr{E}-\mathscr{E}'-i\varepsilon}\sum_\alpha\int d\Omega'\,a_\alpha(\mathscr{E}')\varphi^{(2)}_\alpha$$

has a finite value, so that $\lim_{\varepsilon\to0}\varepsilon J = 0$ (we note that if we evaluate $\hat{G}_2\varphi^{(2)}_{\alpha_0}$ instead of $\hat{G}_2\varphi^{(1)}_{\alpha_0}$, the result becomes $\hat{G}_2\varphi^{(2)}_{\alpha_0} = -\varphi^{(2)}_{\alpha_0}/i\varepsilon$, so that $\lim_{\varepsilon\to+0} i\varepsilon\hat{G}_2\varphi^{(2)}_{\alpha_0} = \varphi^{(2)}_{\alpha_0}$). In view of equation (9.35) we have from (9.34)

$$\varphi = -\frac{1}{H_2-\mathscr{E}'-i0}[V_0(r_1)+V(r_1,r_2)]\varphi \tag{9.37}$$

It follows that $\varphi$ is the solution of the nonhomogeneous equation with the resolvent $\hat{G}_1$ and the solution of the homogeneous equation with the resolvent $\hat{G}_2$.[†] Substitution of equation (9.37) into (9.16) yields

$$w_\alpha^{(2)}(\mathscr{E}, \nu, \mathscr{E}', \nu_0') = -\frac{T_{\alpha_0\alpha}^{(2)}(\mathscr{E}, \nu, \mathscr{E}', \nu_0)}{\mathscr{E}-\mathscr{E}'} \tag{9.38}$$

where

$$T_{\alpha_0\alpha}^{(2)}(\mathscr{E}, \nu, \mathscr{E}', \nu_0)$$
$$= \int \varphi_\alpha^{*(2)}(r_1, r_2, \mathscr{E}, \nu)[V_0(r_1)+V(r_1, r_2)]\varphi(r_1, r_2, \mathscr{E}', \nu_0)\,dr_1\,dr_2 \tag{9.39}$$

Let us now substitute (9.38) into (9.15) and take $t$ to $\pm\infty$. Since according to equation (9.30)

$$\Psi(\mathscr{E}, \nu) = \Psi_{-\alpha_0}^{(1)}(\mathscr{E}, \nu)$$

we have for discrete $\alpha$ and $\alpha_0$

$$\begin{aligned}\Psi_{-\alpha}^{(2)}(\mathscr{E}, \nu) &= 0\\ \Psi_{+\alpha}^{(2)}(\mathscr{E}, \nu) &= -2\pi i \int T_{\alpha_0\alpha}^{(2)}(\mathscr{E}, \nu, \mathscr{E}', \nu_0)\,\Psi_{-\alpha_0}^{(1)}(\mathscr{E}, \nu_0)\,d\Omega'\end{aligned} \tag{9.40}$$

For continuous $\alpha$, corresponding to integration over the continuous spectrum of the atomic states in (9.10), the element $T_{\alpha_0\alpha}^{(2)}$ of the $T$-matrix regarded as a function of $\alpha$ has a singularity of the form $\delta(E_\alpha - \frac{1}{2}k_0^2)$. Consequently, for continuous $\alpha$, $\Psi_{-\alpha}^{(2)}(\mathscr{E}, \nu)$ will also have a singularity. We shall not consider the nature of the singularity here.

Substituting equation (9.40) into (9.12) we obtain the following expression for the $S$-matrix element:

$$S^{2,1}(\mathscr{E}, \nu, \alpha, \mathscr{E}', \nu_0, \alpha_0) = -2\pi i \delta(\mathscr{E}'-\mathscr{E})T_{\alpha_0\alpha}^{(2)}(\mathscr{E}, \nu, \mathscr{E}', \nu_0) \tag{9.41}$$

In order to introduce the symmetry properties of the wave functions let us construct the symmetric and antisymmetric combinations

$$\Psi_s = \frac{1}{\sqrt{2}}(\Psi_\alpha^{(1)} + \Psi_\alpha^{(2)}) \tag{9.42}$$

$$\Psi_a = \frac{1}{\sqrt{2}}(\Psi_\alpha^{(1)} - \Psi_\alpha^{(2)}) \tag{9.43}$$

In view of equations (9.9) and (9.10) it is evident that the state vectors given by the latter two expressions correspond to the symmetric and antisymmetric functions $\Phi$.

Transitions from the initial to the final state for $\Psi_s$ and $\Psi_a$ are described by the symmetrized $S$-matrix which can be constructed from $S^{11}$ and $S^{21}$ by analogy with (9.42) and (9.43):

$$S^+ = (S^{11} + S^{21}) \tag{9.44}$$

$$S^- = (S^{11} - S^{21}) \tag{9.45}$$

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[†] This point is discussed on the basis of the time-independent theory in [26].

From (9.41) and (9.31) we have

$$S^{\pm}(\mathscr{E}, v, \alpha, \mathscr{E}', v_0, \alpha_0) = \delta(\mathscr{E}-\mathscr{E}')\left[\delta(v_0 - v)\delta_{\alpha\alpha_0} - 2\pi i T^{\pm}_{\alpha_0\alpha}(\mathscr{E}, v, \mathscr{E}', v_0)\right] \tag{9.46}$$

where

$$T^{\pm}_{\alpha_0\alpha} = T^{(1)}_{\alpha_0\alpha} \pm T^{(2)}_{\alpha_0\alpha} \tag{9.47}$$

The same result can be obtained in another way. Instead of the functions $\varphi_\alpha^{(1)}$ and $\varphi_\alpha^{(2)}$ we can use as the basis in the interaction representation the symmetric and antisymmetric combinations $(\varphi_\alpha^{(1)} \pm \alpha_\alpha^{(2)}/\sqrt{2}$ normalized to $\delta(\mathscr{E}-\mathscr{E}')\delta(v-v')$, and introduce the symmetrized function

$$\varphi_{\pm} = -\frac{1}{\sqrt{2}} \lim_{\varepsilon\to+0} i\varepsilon\hat{G}(\mathscr{E}+i\varepsilon)(\varphi^{(1)}_{\alpha_0} \pm \varphi^{(2)}_{\alpha_0}) \tag{9.48}$$

which may be rewritten in the form

$$\varphi_{\pm} = \frac{1}{\sqrt{2}}(1 \pm P_{12})\varphi \tag{9.49}$$

where $P_{12}$ is the exchange operator. Consider the integral

$$\frac{1}{\sqrt{2}}\int (\varphi^{(1)}_{\alpha_0} \pm \varphi^{(2)}_{\alpha_0})^* \varphi_{\pm}\, dr_1\, dr_2$$

Using equation (9.49) we have

$$\frac{1}{\sqrt{2}}\int (\varphi^{(1)}_{\alpha_0} \pm \varphi^{(2)}_{\alpha_0})^* \varphi_{\pm}\, dr_1\, dr_2 = \frac{1}{2}\int (1 \pm P_{12})\varphi^{(1)*}_{\alpha_0}(1 \pm P_{12})\varphi\, dr_1\, dr_2 \tag{9.50}$$

However,

$$\begin{aligned}\int (1 \pm P_{12})\varphi^{(1)*}_{\alpha_0}(1 \pm P_{12})\varphi\, dr_1\, dr_2 &= \int \varphi(1 \pm P_{12})^2 \varphi^{(1)*}_{\alpha_0}\, dr_1\, dr_2 \\ &= 2\int \varphi(1 \pm P_{12})\varphi^{(1)*}_{\alpha_0}\, dr_1\, dr_2\end{aligned} \tag{9.51}$$

and therefore

$$\begin{aligned}\frac{1}{\sqrt{2}}\int (\varphi^{(1)}_{\alpha_0} \pm \varphi^{(2)}_{\alpha_0})^* \varphi_{\pm}\, dr_1\, dr_2 &= \int (\varphi^{(1)}_{\alpha_0} \pm \varphi^{(2)}_{\alpha_0})^* \varphi\, dr_1\, dr_2 \\ &= \int \varphi^{(1)*}_{\alpha_0}\varphi\, dr_1\, dr_2 \pm \int \varphi^{(2)*}_{\alpha_0}\varphi\, dr_1\, dr_2\end{aligned} \tag{9.52}$$

This corresponds to the representation of the matrix $T^{\pm}_{\alpha_0\alpha}$ in the form given by (9.47). It is possible to establish a relation between $T^{\pm}_{\alpha_0\alpha}$ and the effective cross-section by analogy with § 1. But it must be remembered that the symmetrized wave functions correspond to the superposition of two physically identical situations: scattering of the first electron by the atom containing the second electron, and scattering of the second electron by the atom containing the first electron. The expression for the differential cross-section for elastic scattering is of the form

$$d\sigma^{\pm}_{\alpha_0\alpha_0} = (2\pi)^4 \frac{1}{k_0^2}\left|T^{\pm}_{\alpha_0\alpha_0}\right|^2 d\Omega \tag{9.53}$$

while the expression for the differential cross-section for inelastic scattering in which the atom undergoes a transition from the state $\alpha_0$ to the state $\alpha$ is

$$d\sigma^{\pm}_{\alpha_0\alpha} = (2\pi)^4 \frac{1}{k_0^2}\left|T^{\pm}_{\alpha_0\alpha}\right|^2 d\Omega \tag{9.54}$$

When comparing theory with experiment it must be remembered that in practice one is usually dealing with the scattering of an unpolarized beam of electrons forming a statistical mixture. Accordingly, equation (9.54) must be averaged over the triplet and singlet states. The result is

$$\langle d\sigma_{\alpha_0\alpha}\rangle = \tfrac{3}{4}d\sigma^{-}_{\alpha_0\alpha}+\tfrac{1}{4}d\sigma^{+}_{\alpha_0\alpha} \tag{9.55}$$

There is an important relation between the elastic and inelastic scattering cross-sections which is a consequence of the unitarity of the $S$-matrix and forms a generalization of the optical theorem given by (1.48). The matrices $S^{+}$ and $S^{-}$ are unitary, i.e. they obey a relation analogous to equation (1.7):

$$\sum_{\alpha}\int S^{\pm *}(\mathscr{E},\alpha,\nu,\mathscr{E}',\alpha',\nu')S^{\pm}(\mathscr{E},\alpha,\nu,\mathscr{E}'',\alpha'',\nu'')\,d\mathscr{E}\,d\Omega = \delta(\mathscr{E}'-\mathscr{E}'')\,\delta(\nu''-\nu')\,\delta_{\alpha'\alpha''} \tag{9.56}$$

With the aid of (9.46) we can use the unitary property to deduce a relation analogous to (1.48), namely

$$-\operatorname{Im} T^{\pm}_{\alpha_0\alpha_0}(0) = \pi\sum_{\alpha}\int\left|T^{\pm}_{\alpha_0\alpha}\right|^2 d\Omega \;{}^{\dagger} \tag{9.57}$$

In this formula the summation is carried out only over those levels which can be excited at a given energy in accordance with equation (9.32). When the initial state of the atoms is the ground state and the energy of the incident electron is insufficient for excitation of the atom, the sum in (9.57) consists of one term only.

The $S$-matrix is also invariant with respect to time reversal. This leads to a generalization of equation (1.8) and may be written in the form

$$S^{\pm}_{\alpha_0\alpha}(\mathscr{E},\nu,\mathscr{E}',\nu_0) = S^{\pm}_{\alpha\alpha_0}(\mathscr{E}',-\nu_0,\mathscr{E},-\nu) \tag{9.58}$$

Accordingly, we have the following relation for the $T$-matrix elements

$$T^{\pm}_{\alpha_0\alpha}(\mathscr{E},\nu,\mathscr{E},\nu_0) = T^{\pm}_{\alpha\alpha_0}(\mathscr{E},-\nu_0,\mathscr{E},-\nu) \tag{9.59}$$

It is understood that in the time-reversed transition described by the right-hand sides of (9.58) and (9.59), the signs of the orbital and spin angular momenta have been reversed. The transition of an atom from one state to another which we have been considering is, in fact, invariant with respect to reversal of all the components of the angular and linear momenta. It follows that we can use equations (9.59) and (9.54) to write down the detailed-balance relation:

$$k_0^2\,d\sigma_{\alpha_0\alpha} = k_\alpha^2\,d\sigma_{\alpha\alpha_0} \tag{9.60}$$

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† $T^{\pm}_{\alpha_0\alpha_0}(0)$ represents $T^{\pm}_{\alpha_0\alpha_0}(\mathscr{E},\nu_0,\mathscr{E},\nu_0)$.

## 10. EQUATIONS FOR THE WAVE FUNCTION OF THE SCATTERED ELECTRON

If the eigenfunction $\varphi(r_1, r_2)$ of the energy operator for the atom + electron system is expanded in terms of the atomic functions $\varphi_\alpha(r_1)$, the set of expansion coefficients will represent the wave function of the scattered electron.

In this section we shall establish the equations and asymptotic behaviour for the wave function of the scattered electron.

To start with, let us change the normalization by multiplying $\varphi$ and $\varphi_\pm$ by $(2\pi)^{\frac{3}{2}}k_0^{-\frac{1}{2}}$. The corresponding functions will be denoted by $\psi$ and $\psi_\pm$. For the $\psi$ functions we have the integral equation

$$\psi(r_1, r_2) = -\lim_{\varepsilon\to+0} i\varepsilon\hat{G}(\mathscr{E}+i\varepsilon)\, e^{ik_0\nu_0\cdot r_2}\,\psi_{\alpha_0}(r_1) \tag{10.1}$$

As has been shown above, from equation (10.1) can be obtained two integral equations (one through the resolvent $\hat{G}_1$ and the other through $\hat{G}_2$):

$$\psi(r_1, r_2) = e^{ik_0\nu_0\cdot r_2}\,\psi_{\alpha_0}(r_1) - \hat{G}_1(\mathscr{E}+i0)[V_0(r_2)+V(r_1, r_2)]\psi \tag{10.2}$$

$$\psi(r_1, r_2) = -\hat{G}_2(\mathscr{E}+i0)[V_0(r_1)+V(r_1, r_2)]\psi \tag{10.3}$$

or, using Green's functions

$$\psi(r_1, r_2) = e^{ik_0\nu_0\cdot r_2}\,\psi_{\alpha_0}(r_1) - \\ -\int G_1(r_1, r_2, r_1', r_2')[V_0(r_2')+V(r_1', r_2')]\psi(r_1', r_2')\,dr_1'\,dr_2' \tag{10.4}$$

$$\psi(r_1, r_2) = -\int G_2(r_1, r_2, r_1', r_2')[V_0(r_1')+V(r_1', r_2')]\psi(r_1', r_2')\,dr_1'\,dr_2' \tag{10.5}$$

The latter equations may be used to investigate the asymptotic behaviour of $\psi(r_1, r_2)$, as follows. Consider the asymptotic behaviour of the Green's functions $G_1$ and $G_2$. These two functions are expressed in terms of the free-motion function $G_0$. By expanding $G_1$ and $G_2$ in terms of the eigenfunctions of $H_1$ and $H_2$, it is easy to show that

$$G_1(r_1, r_2, r_1', r_2') = \sum_\alpha \psi_\alpha(r_1)\psi_\alpha^*(r_1')G_0(k_\alpha, r_2, r_2') \tag{10.6}$$

and

$$G_2(r_1, r_2, r_1', r_2') = \sum_\alpha \psi_\alpha(r_2)\psi_\alpha^*(r_2')G_0(k_\alpha, r_1, r_1') \tag{10.7}$$

where

$$\left.\begin{aligned} G_0(k_\alpha, r, r') &= -\frac{1}{2\pi|r-r'|}\,e^{ik_\alpha|r-r'|} \\ k_\alpha &= \sqrt{2(E_{\alpha_0}-E_\alpha)+k_0^2} \end{aligned}\right\} \tag{10.8}$$

When $r \gg r'$

$$G_0 \sim -\frac{1}{2\pi r}\,e^{ik_\alpha r}\,e^{-ik_\alpha n\cdot r'} \tag{10.9}$$

For those values of $\alpha$ for which $E_{\alpha_0}+\frac{1}{2}k_0^2 < E_\alpha$, the function $G_0(r)$ falls off as $\exp(-|k_\alpha|r)$. Substituting equation (10.9) into (10.6) and (10.7) and retaining only those terms in the sum in which $k_\alpha$ is real, we have

$$G_1 \underset{r_2\to\infty}{\sim} \frac{1}{2\pi}\sum_{k_\alpha{}^2>0} \psi_\alpha(r_1)\psi_\alpha^*(r_1')\frac{e^{ik_\alpha r_2}}{r_2}e^{-ik_\alpha n.r_2'} \tag{10.10}$$

Substituting equation (10.10) into (10.4) and (10.6),

$$\psi\underset{r_2\to\infty}{(r_1,r_2)} \sim \left(e^{ik_0 v_0.r_2}+f_{\alpha_0\alpha_0}\frac{e^{ik_0 r_2}}{r_2}\right)\psi_{\alpha_0}(r_1)+\sum_{(k_\alpha^2>0)} f_{\alpha_0\alpha}\frac{e^{ik_\alpha r_2}}{r_2}\psi_\alpha(r_1) \tag{10.11}$$

where

$$f_{\alpha_0\alpha} = -\frac{1}{2\pi}\int e^{-ik_\alpha n.r_2'}\psi_\alpha^*(r_1')[V_0(r_2')+V(r_1',r_2')]\psi(r_1',r_2')\,dr_1'\,dr_2' \tag{10.12}$$

When $r_1 \to \infty$,

$$\psi\underset{r_1\to\infty}{(r_1,r_2)} \sim \sum_{(k_\alpha{}^2>0)} g_{\alpha_0\alpha}\frac{e^{ik_\alpha r_1}}{r_1}\psi_\alpha(r_2) \tag{10.13}$$

where

$$g_{\alpha_0\alpha} = -\frac{1}{2\pi}\int e^{-ik_\alpha n.r_1'}\psi_\alpha^*(r_1')[V_0(r_1')+V(r_1',r_2')]\psi(r_1',r_2')]\,dr_1'\,dr_2' \tag{10.14}$$

Comparison of equations (10.12), (10.14) with (9.29) and (9.39) yields the relation between $f_{\alpha_0\alpha}$, $g_{\alpha_0\alpha}$ and $T^{(1)}_{\alpha_0\alpha}$, $T^{(2)}_{\alpha_0\alpha}$:

$$T^{(1)}_{\alpha_0\alpha}(\mathscr{E},n,\mathscr{E},v_0) = -\frac{1}{(2\pi)^2}k_0^{\frac{1}{2}}k_\alpha^{\frac{1}{2}}f_{\alpha_0\alpha}(n,v_0) \tag{10.15}$$

$$T^{(2)}_{\alpha_0\alpha}(\mathscr{E},n,\mathscr{E},v_0) = -\frac{1}{(2\pi)^2}k_0^{\frac{1}{2}}k_\alpha^{\frac{1}{2}}g_{\alpha_0\alpha}(n,v_0) \tag{10.16}$$

Let us now expand $\psi(r_1, r_2)$ in terms of the atomic functions:

$$\psi(r_1,r_2) = \sum_\alpha \psi_\alpha(r_1)F_\alpha(r_2) \tag{10.17}$$

where the symbol $\sum_\alpha$ includes integration over the continuous spectrum. We substitute equations (10.17) and (10.6) into (10.4), multiply by $\psi_\alpha^*$ and integrate. For the coefficients $F_\alpha(r_2)$ which represent the wave function of the scattered electron we then have the set of equations

$$F_\alpha(r_2) = e^{ik_0 v_0.r_2}\delta_{\alpha_0\alpha}+\sum_{\alpha'}\int \psi_\alpha^*(r_1')[V_0(r_2')+V(r_1',r_2')]$$
$$\times\psi_{\alpha'}(r_1')G_0(k_\alpha,r_2,r_2')F_{\alpha'}(r_2')\,dr_1'\,dr_2' \tag{10.18}$$

where the integration is with respect to $r_1'$. Let

$$V_{\alpha\alpha'}(r_2) = \int \psi_\alpha^*(r_1)[V_0(r_2)+V(r_1,r_2)]\psi_{\alpha'}(r_1)\,dr_1 \tag{10.19}$$

Using the explicit form of $V_0(r_2)$ and $V(r_1, r_2)$ given by (9.2), we obtain

$$V_{\alpha\alpha'}(r_2) = -\frac{1}{r_2}\delta_{\alpha\alpha'}+\int\frac{\psi_\alpha^*(r_1)\psi_{\alpha'}(r_1)}{|r_2-r_1|}dr_1 \tag{10.20}$$

Substituting (10.20) into (10.18), we obtain

$$F_\alpha(r) = e^{ik_0 v_0 \cdot r}\delta_{\alpha_0\alpha} + \sum_{\alpha'} \int G_0(k_\alpha, r, r')V_{\alpha\alpha'}(r')F_\alpha(r')\,dr' \tag{10.21}$$

where the subscript 2 has been omitted. This system of integral equations is equivalent to the set of differential equations

$$\Delta F_\alpha + (k_\alpha^2 - 2V_{\alpha\alpha})F_\alpha = 2\sum_{\alpha' \neq \alpha} V_{\alpha\alpha'}F_{\alpha'} \tag{10.22}$$

with the asymptotic condition

$$F_\alpha = e^{ik_0 v_0 \cdot r}\delta_{\alpha_0\alpha} + f_{\alpha_0\alpha}\frac{e^{ik_\alpha r}}{r} \qquad r \to \infty \tag{10.23}$$

The system given by (10.22) can also be obtained by substituting the expansion given by (10.17) into

$$\int \psi_\alpha^*(r_1)(H - \mathscr{E})\psi(r_1, r_2)\,dr_1 = 0 \tag{10.24}$$

It is shown in [17] that the latter relation is a consequence of the fact that the functional

$$I = \sum_{\alpha'} \int \psi_\alpha^*(r_1)(H - \mathscr{E})\psi_{\alpha'}(r_1)F_{\alpha'}(r_2)\,dr_1\,dr_2 \tag{10.25}$$

is stationary with respect to arbitrary variations of $F_{\alpha'}$ which vanish when $r_2 \to \infty$. On this basis we shall suppose that equation (10.24) is valid even when $\psi(r_1, r_2)$ is not an exact solution of $(H - \mathscr{E})\psi = 0$ but represents an approximate expression, for example, the sum of a finite number of terms in (10.17). This leads to the equations for $F_\alpha$ which give the best approximation in the variational sense.

Consider the part of the sum in (10.17) which corresponds to the continuous spectrum. It is given by the integral

$$J(r_1, r_2) = \int F(\kappa, k, r_2)\psi(\kappa, r_1)\,d\kappa \tag{10.26}$$

There is also a relation between $k$ and $\kappa$ which follows from the law of conservation of energy

$$k^2 + \kappa^2 = k_0^2 + 2E_{\alpha_0} \tag{10.27}$$

It turns out that $F(\kappa, k, r)$ in (10.24) has a singularity at $\kappa^2 = k_0^2$ [27]. Let us consider the nature of this singularity in greater detail and expand $F_\alpha$ in terms of $\psi$:

$$F_\alpha = \sum_{\alpha'} c_{\alpha\alpha'}\psi_{\alpha'} \tag{10.28}$$

Substitution of this expansion into (10.22) yields

$$\sum_{\alpha'} c_{\alpha\alpha'}(\Delta + k_{\alpha'}^2 - 2V_{\alpha\alpha})\psi_{\alpha'} = 2\sum_{\lambda, \beta \neq \alpha} c_{\beta\lambda}V_{\alpha\beta}\psi_\lambda \tag{10.29}$$

The function $\psi_{\alpha'}$ satisfies the equation

$$\Delta\psi_{\alpha'} = -2\left(E_{\alpha'} + \frac{1}{r}\right)\psi_{\alpha'} \tag{10.30}$$

From the latter equation and from equation (10.21) we have

$$\sum_{\alpha'} c_{\alpha\alpha'}(k_\alpha^2-2E_{\alpha'})\psi_{\alpha'} = 2\sum_{\beta,\lambda}\left(\frac{1}{|r-r'|}\right)_{\beta\alpha} c_{\beta\lambda}\psi_\lambda \tag{10.31}$$

Multiplying $\psi_{\alpha_0}^*$ and integrating,

$$c_{\alpha\alpha_0}(k_\alpha^2-2E_{\alpha_0}) = 2\sum_{\beta,\lambda} c_{\beta\lambda}\left(\frac{1}{|r-r'|}\right)_{\beta\alpha}\psi_\lambda \tag{10.32}$$

Substituting $\alpha = \alpha_0$ and using (10.27),

$$c_{\alpha_0}(\kappa)(k_0^2-\kappa^2) = 2\sum_{\beta,\lambda} c_{\beta\lambda}\int \psi_\beta^*(r_1)\psi_0^*(r_2)\psi_\alpha(r_1)\psi_\lambda(r_2)\frac{1}{|r_1-r_2|}\,dr_1\,dr_2 \tag{10.33}$$

In order to avoid complications connected with the specific asymptotic behaviour of continuous-spectrum Coulomb functions, we shall cut off the Coulomb interaction by introducing the factor $\exp(-\omega r)$ where $\omega$ is a finite positive number which can be as small as desired. The right-hand side of (10.33) will then be finite for $k_0 = \kappa$, so that

$$c_{\alpha_0}(\kappa) = \frac{\text{const}}{k_0^2-\kappa^2} \tag{10.34}$$

Therefore, $F(\kappa, \mathbf{r})$ can be written in the form

$$F(\kappa, \mathbf{r}) = \frac{A}{k_0^2-\kappa^2}\psi_{\alpha_0}(\mathbf{r})+B(\mathbf{r}) \tag{10.35}$$

where $B(r)$ is a function having no singularity at $k_0 = \kappa$.

When we substitute equation (10.35) into (10.26) we must determine the path of integration with respect to $\kappa$. This can be found from the asymptotic form of $\psi(r_1, r_2)$ given by equation (10.15) when $r_1 \to \infty$. We substitute (10.35) into (10.26) and separate the angular variables. Assuming that $r_1$ is large, the radial part $\psi_l(\kappa, r_2)$ has the asymptotic form

$$\psi_l(r) \sim \frac{1}{r}\sin\left(\kappa r - \frac{l\pi}{2} + \delta_l\right) \tag{10.36}$$

so that

$$J_l(r_1, r_2) \sim \frac{\text{const}}{r_1}\psi_{\alpha_0}(r_2)\int_0^\infty \frac{\sin\left(\kappa r_1 - \frac{l\pi}{2} + \delta_l\right)}{(k_0^2-\kappa^2)}\kappa^2\,d\kappa \tag{10.37}$$

can be reduced to the form

$$J \sim \text{const}\,\psi_{\alpha_0}(r_2)\frac{1}{r_1}\int_{-\infty}^{\infty}\frac{e^{i\kappa r_1}}{k_0^2-\kappa^2}\kappa^2\,d\kappa \tag{10.38}$$

The path of integration can now be chosen so that the pole $\kappa = k_0$ is excluded by taking a small circle around it in the upper half-plane, while the pole $\kappa_0 = -k_0$ is excluded using a circle in the lower half-plane of complex $\kappa$.

The result is

$$J \sim \text{const}\, \psi_{\alpha_0}(r_2) \frac{e^{ik_0 r_1}}{r_1} \tag{10.39}$$

In the absence of a purely Coulomb field the divergence will be of the form $(k_0^2-\kappa^2)^{-1+i/\kappa}$ instead of $(k_0^2-\kappa^2)^{-1}$, and instead of the asymptotic form (10.36) it will have the Coulomb form:

$$\psi = \frac{1}{r}\sin\left[\kappa r - \frac{l\pi}{2} + \frac{1}{\kappa}\ln 2\kappa r + \arg\Gamma\left(l+1-\frac{i}{\kappa}\right)\right]$$

The analysis is then very much more complicated and has not in fact been completed. However, the general result will be similar to that in the simpler case of a truncated Coulomb interaction.

Let us now consider symmetrized function $\psi_\pm$. As with equation (9.49), this function can be obtained by applying the operator $\frac{1}{\sqrt{2}}(1 \pm P_{12})$ to the function $\psi$

$$\psi_\pm = \frac{1}{\sqrt{2}}\psi \pm \frac{1}{\sqrt{2}}P_{12}\psi \tag{10.40}$$

We now deduce the integral equation for $\psi_\pm$, transforming the first component on the right-hand side of equation (10.40) using the inhomogeneous equation (10.2), whilst the second component will be transformed with the aid of the homogeneous equation (10.3). Since $P_{12}\hat{G}_2 = \hat{G}_1$ and $P_{12}V_0(r_2) = V_0(r_1)$,

$$\psi_\pm = \frac{1}{\sqrt{2}} e^{ik_0 v_0 . r_2}\psi_{\alpha_0}(r_1) - \int G_1(r_1, r_2, r_1', r_2') \times [V_0(r_2') + V(r_1', r_2')]\psi_\pm(r_1', r_2')\, dr_1'\, dr_2' \tag{10.41}$$

Using the expansion (10.6) for the Green's function,

$$\psi_\pm = \frac{1}{\sqrt{2}} e^{ik_0 v_0 . r_2}\psi_{\alpha_0}(r_1) - \sum_\alpha \psi_\alpha(r_1) \int \psi_\alpha^*(r_1') \times [V_0(r_2') + V(r_1', r_2')]G_0(k_\alpha, r_2, r_2')\psi_\pm(r_1', r_2')\, dr_1'\, dr_2' \tag{10.42}$$

from which we obtain the asymptotic behaviour of $\psi_\pm$ for large $r_2$:

$$\psi_\pm = \psi_{\alpha_0}(r_1)\left(\frac{1}{\sqrt{2}} e^{ik_0 v_0 . r_2} + q^\pm_{\alpha_0\alpha_0}\frac{e^{ik_0 r_2}}{\sqrt{2}r_2}\right) + \sum_{\alpha \neq \alpha_0} q^\pm_{\alpha_0\alpha}\psi_\alpha(r_1)\frac{e^{ik_\alpha r_2}}{\sqrt{2}r_2} \tag{10.43}$$

where

$$q^\pm_{\alpha_0\alpha} = -\frac{\sqrt{2}}{2\pi}\int e^{-ik_\alpha n . r_2'}\psi_\alpha^*(r_1')[V_0(r_2') + V(r_1', r_2')]\psi_\pm(r_1', r_2')\, dr_1'\, dr_2' \tag{10.44}$$

Writing $\psi_\pm$ in the form $\psi_\pm = \frac{1}{\sqrt{2}}[\psi(r_1, r_2) \pm \psi(r_2, r_1)]$, and bearing in mind (10.13) and (10.15), we have

$$q^\pm_{\alpha_0\alpha} = f^\alpha_{\alpha_0\alpha} \pm g^\alpha_{\alpha_0\alpha} \tag{10.45}$$

We might expand $\psi_\pm$ in terms of the atomic functions, writing it in the form of (10.19). However, in this form the symmetry properties of $\psi_\pm$ are difficult to see (they are ensured by that part of the expansion which refers to the continuous spectrum). Instead we write $\psi_\pm$ in a form in which the symmetry properties are immediately evident:

$$\psi_\pm = \frac{1}{\sqrt{2}} \sum_\alpha [F_\alpha^\pm(r_2)\psi_\alpha(r_1) \pm F_\alpha^\pm(r_1)\psi_\alpha(r_2)] \tag{10.46}$$

This representation has an important property: it is invariant with respect to the transformation

$$F_\alpha^\pm(r) \to F_\alpha^\pm(r) + \sum_\beta D_{\alpha\beta}^\pm \psi_\beta$$

where $D_{\alpha\beta}^\pm$ is symmetric or antisymmetric, depending on which of the two signs is taken:

$$D_{\alpha\beta}^\pm = \pm D_{\beta\alpha}^\pm$$

This result may be used to remove the singularity in $F_\kappa^\pm(r)$ in the integral over the continuous spectrum which is contained in (10.46) (this does not, however, define $F_\alpha^\pm$ unambiguously). We now proceed to derive the equations for $F_\alpha^\pm$. Substituting equation (10.46) into (10.42), multiplying by $\psi_\alpha^*(r_1)$ and integrating with respect to $r_1$, we obtain

$$\begin{aligned} F_\alpha^\pm(r_2) = {} & \mp \sum_{\alpha'} \psi_\alpha(r_2) \int \psi_\alpha^*(r_1) F_{\alpha'}^\pm(r_1)\, dr_1 + e^{ik_0 v_0 . r_2} \delta_{\alpha\alpha_0} - \\ & - \sum_{\alpha'} \int \psi_\alpha^*(r_1')[V_0(r_2') + V(r_1', r_2')]\psi_{\alpha'}(r_1') F_{\alpha'}^\pm(r_2') \\ & \times G_0(k_\alpha, r_2, r_2')\, dr_1'\, dr_2' \mp \sum_{\alpha'} \int \psi_\alpha^*(r_1')[V_0(r_2') + V(r_1', r_2')] \\ & \times \psi_{\alpha'}(r_2') F_{\alpha'}^\pm(r_1') G_0(k_\alpha, r_2, r_2')\, dr_1'\, dr_2' \end{aligned} \tag{10.47}$$

This equation can be transformed to a more convenient form. Consider the following part of the last term on the right-hand side of equation (10.47):

$$J = \mp \sum_{\alpha'} \int G_0(k_\alpha, r_2, r_2') V_0(r_2') \psi_{\alpha'}(r_2')\, dr_2' \int \psi_\alpha^*(r_1') F_{\alpha'}^\pm(r_1')\, dr_1' \tag{10.48}$$

Using equation

$$-\tfrac{1}{2}\Delta_2' \psi_{\alpha'} + V_0(r_2')\psi_{\alpha'} = E_{\alpha'} \psi_{\alpha'}$$

we can rewrite (10.48) in the form

$$J = \mp \sum_{\alpha'} \int (\tfrac{1}{2}\Delta_2' + E_\alpha') \psi_{\alpha'}(r_2') G_0(k_\alpha, r_2, r_2')\, dr_2' \int \psi_\alpha^*(r_1') F_{\alpha'}^\pm(r_1')\, dr_1' \tag{10.49}$$

and hence, bearing in mind the explicit form of $G_0$ given by (2.7), we have after some rearrangement

$$J = \pm \sum_{\alpha'} \left[\psi_{\alpha'}(r_2) + \int (\tfrac{1}{2}k_\alpha^2 - E_{\alpha'}) G_0(k_\alpha, r_2, r_2')\, dr_2'\right] \int \psi_\alpha^*(r_1') F_{\alpha'}^\pm(r_1')\, dr_1' \tag{10.50}$$

The term

$$\mp \sum_{\alpha'} \psi_{\alpha'}(r_2) \int \psi_\alpha^*(r_1') F_{\alpha'}^\pm(r_1')\, dr_1'$$

is of exactly the same form as the first term on the right-hand side of equation (10.47) but with the opposite sign; therefore they cancel out. It follows that we can reduce (10.47) to the form

$$F_\alpha^\pm(r_2) = e^{ik_0 v_0 \cdot r_2}\,\delta_{\alpha\alpha_0} - \sum_{\alpha'} \int G_0(k_\alpha, r_2, r_2')V_{\alpha\alpha'}(r_2')F_{\alpha'}^\pm(r_2')\,dr_2' - \sum_{\alpha'} \int G_0(k_\alpha, r_2, r_2')\,dr_2' \int W_{\alpha\alpha'}^\pm(r_1', r_2')F_{\alpha'}^\pm(r_1')\,dr_1' \tag{10.51}$$

where $V_{\alpha\alpha'}$ is given by (10.20) and $W_{\alpha\alpha'}^\pm$ represents the kernel of the exchange operator

$$W_{\alpha\alpha'}^\pm(r_1, r_2) = \pm\psi_\alpha^*(r_1)[V(r_1, r_2) + E_{\alpha'} - \tfrac{1}{2}k_\alpha^2]\psi_{\alpha'}(r_2) \tag{10.52}$$

On reversing the order of integration in (10.51) and substituting

$$K_{\alpha\alpha'}^\pm(r_2, r_2') = -V_{\alpha\alpha'}(r_2')G_0(k_\alpha, r_2, r_2') - \int W_{\alpha\alpha'}^\pm(r_1', r_2')G_0(k_\alpha, r_2, r_1')\,dr_1' \tag{10.53}$$

we have finally

$$F_\alpha^\pm(r_2) = e^{ik_0 v_0 \cdot r_2}\,\delta_{\alpha_0\alpha} + \sum_{\alpha'} \int K_{\alpha\alpha'}^\pm(r_2, r_2')F_{\alpha'}^\pm(r_2')\,dr_2' \tag{10.54}$$

The integral equations (10.51) and (10.54) are equivalent to the following system of integro-differential equations

$$\Delta F_\alpha^\pm + (k_\alpha^2 - 2V_{\alpha\alpha})F_\alpha^\pm - 2\int W_{\alpha\alpha}^\pm(r', r)F_\alpha(r')\,dr' = 2\sum_{\alpha' \neq \alpha}\left(V_{\alpha\alpha'}F_{\alpha'}^\pm + \int W_{\alpha\alpha'}^\pm F_{\alpha'}^\pm\,dr'\right) \tag{10.55}$$

with the asymptotic conditions

$$F_\alpha^\pm(r) \underset{r\to\infty}{\sim} e^{ik_0 v_0 \cdot r}\,\delta_{\alpha\alpha_0} + q_{\alpha_0\alpha}^\pm(n, v_0)\frac{e^{ik_\alpha r}}{r} \tag{10.56}$$

In the ensuing analysis we shall, in view of equation (10.55), look upon the term $V_{\alpha\alpha'}F_{\alpha'}^\pm + \int W_{\alpha\alpha'}^\pm F_{\alpha'}^\pm\,dr'$ for $\alpha \neq \alpha'$ as expressing the relation between the states $\alpha$ and $\alpha'$.

Utilizing equations (10.54) and (10.16) we have

$$T_{\alpha_0\alpha}^\pm(\mathscr{E}, n, \mathscr{E}, v_0) = -\frac{1}{(2\pi)^2}k_0^{\frac{1}{2}}k_\alpha^{\frac{1}{2}}q_{\alpha_0\alpha}^\pm(n, v_0) \tag{10.57}$$

Substitution of (10.57) into (9.54) yields the following expression for the inelastic scattering cross-section

$$d\sigma_{\alpha_0\alpha}^\pm = \frac{k_\alpha}{k_0}|q_{\alpha_0\alpha}^\pm|^2\,d\Omega \tag{10.58}$$

The differential cross-section for elastic scattering can be obtained from this by substituting $\alpha = \alpha_0$:

$$d\sigma_{\alpha_0\alpha_0}^\pm = |q_{\alpha_0\alpha_0}^\pm|^2\,d\Omega \tag{10.59}$$

These expressions can also be obtained directly from the asymptotic form (10.56) by dividing the flux in the solid angle $d\Omega$ (i.e. $k_\alpha|q_{\alpha_0\alpha}^\pm|^2\,d\Omega$), by the flux density in the incident wave $k_0$.

On substituting (10.57) into the unitarity condition (9.57),

$$\frac{4\pi}{k_0}\operatorname{Im} q^{\pm}_{\alpha_0\alpha}(0) = \sum_{\alpha} \frac{k_\alpha}{k_0} \int |q^{\pm}_{\alpha_0\alpha}|^2 \, d\Omega \tag{10.60}$$

The quantity

$$\sigma^{\pm} = \sum_{\alpha} \sigma^{\pm}_{\alpha_0\alpha} = \sum_{\alpha} \frac{k_\alpha}{k_0} \int |q^{\pm}_{\alpha_0\alpha}|^2 \, d\Omega \tag{10.61}$$

is the total cross-section for all the elastic and inelastic processes possible at the given energy. Therefore,

$$4\pi \operatorname{Im} q^{\pm}_{\alpha_0\alpha_0}(0) = k\sigma^{\pm} \tag{10.62}$$

## 11. EQUATIONS FOR THE PARTIAL WAVES

Let us separate the angular variables in equations (10.55) and (10.56) and expand $F^{\pm}_{\alpha}$ in terms of the spherical harmonics as in § 2. In order to distinguish the quantum numbers associated with the angular momenta of the atomic and incident electrons, we write $l_1$, $\mu_1$ for the atomic and $l_2$, $\mu_2$ for the incident electrons, respectively. The symbol $n$ represents the principal quantum number and the symbols $\pm$ will be omitted. With all the indices written out in full, the expansion is

$$F_{nl_1\mu_1}(r) = \sum_{l_2} \sqrt{4\pi(2l_2+1)}\, i^{l_2} \frac{f^{l_2\mu_2}_{nl_1\mu_1}}{r} Y_{l_2\mu_2}(\theta, \varphi) \tag{11.1}$$

The summation over $\mu_2$ is unnecessary in view of the conservation of the $z$-component of the angular momentum of the atom + electron system:

$$\mu_1 + \mu_2 = \text{const}$$

Since the $z$-component of the angular momentum of the incident electron in the initial state is $\mu_2^0 = 0$ it follows that $\mu_1 + \mu_2 = \mu_1^0$. If we now substitute equation (11.1) into (10.56), multiply by $Y^*_{l_2^0 0}(\theta, \varphi)$ and integrate, we obtain the following asymptotic expression for $f^{l_2\mu_2}_{nl_1\mu_1}$:

$$f^{l_2\mu_2}_{nl_1\mu_1} \sim \frac{1}{k_{n_0}} \sin\left(k_{n_0} r - \frac{l_2^0 \pi}{2}\right) \delta_{nn_0} \delta_{l_1 l_1^0} \delta_{\mu_1\mu_2^0} + q^{l_2^0 0 l_2\mu_2}_{n_0 l_1^0 \mu_1^0 n l_1 \mu_1} \frac{e^{i\left(k_n r - \frac{l_2\pi}{2}\right)}}{r} \tag{11.2}$$

where

$$q^{l_2^0 0 l_2\mu_2}_{n_0 l_1^0 \mu_1^0 n l_1 \mu_1} = \int Y^*_{l_2^0 0}\, q_{n_0 l_1^0 \mu_1^0 n l_1 \mu_1}(v_0, n) Y_{l_2\mu_2}\, d\Omega \tag{11.3}$$

Next, let us substitute equation (11.1) into (10.55), multiply by $Y^*_{l_2'\mu_2'}(\theta, \varphi)$ and integrate with respect to the angles. It will also be convenient to substitute

$$\mathscr{V}^{\,l_2\mu_2 l_2'\mu_2'}_{nl_1\mu_1 n'l_1'\mu_1'} = \int Y_{l_2\mu_2}(\theta, \varphi) V_{\alpha\alpha'}(r) Y^*_{l_2'\mu_2'}(\theta, \varphi)\, d\Omega \tag{11.4}$$

and

$$\mathscr{W}^{\,l_2\mu_2 l_2'\mu_2'}_{nl_1\mu_1 n'l_1'\mu_1'}(r', r) = r', r \int Y_{l_2\mu_2}(\theta', \varphi') W_{\alpha\alpha'}(r', r) Y^*_{l_2'\mu_2'}(\theta, \varphi)\, d\Omega\, d\Omega' \tag{11.5}$$

In view of the presence of $|r - r'|^{-1}$ in $W_{\alpha\alpha'}$, the form of (11.5) will be different for $r \leqslant r'$ and $r \geqslant r'$. In order to take this into account, we shall use the symbol $\mathscr{W}^{(1)}$ for $r \leqslant r'$ and $\mathscr{W}^{(2)}$ for $r \geqslant r'$. The system of equations (10.55) will then be of the form

$$\frac{d^2 f^{l_2\mu_2}_{nl_1\mu_1}}{dr^2} + \left(k_n^2 - \frac{l_2(l_2+1)}{r^2}\right) f^{l_2\mu_2}_{nl_1\mu_1}$$

$$= 2 \sum_{n'l_1'l_2'\mu_1'} \left[ \mathscr{V}^{l_2\mu_2 l_2'\mu_2'}_{nl_1\mu_1 n'l_1'\mu_1'} f^{l_2'\mu_2'}_{n'l_1'\mu_1'} + \int\limits_0^\infty \mathscr{W}^{l_2\mu_2 l_2'\mu_2'}_{nl_1\mu_1 n'l_1'\mu_1'} f^{l_2'\mu_2'}_{n'l_1'\mu_1'} \, dr' \right] \tag{11.6}$$

where $f^{l_2\mu_2}_{nl_1\mu_1}(0) = 0$ when $r = 0$.

The function $f^{l_2\mu_2}_{nl_1\mu_1}$ describes the state of both electrons on the $l_1, \mu_1, l_2, \mu_2$ representation. It is convenient to replace this by the $l_1, l_2, L, M$ representation, where $L$ is the total angular momentum and $M$ its $z$-component (this is known as the total angular momentum representation [28]). Since in the nonrelativistic theory the angular momentum is a constant of motion, on the total angular momentum representation the system of equations (11.6) splits into a series of unconnected sub-systems. The transition from one representation to the other is carried out with the aid of the transformation

$$\tilde{f}^{LM}_{nl_1l_2} = \sum_{\mu_1,\mu_2} C^{LM}_{l_1\mu_1l_2\mu_2} f^{l_2\mu_2}_{nl_1\mu_1} \tag{11.7}$$

where $C^{LM}_{l_1\mu_1l_2\mu_2}$ are the Clebsch-Gordon coefficients. Substituting equation (11.7) into the asymptotic expression (11.6),

$$\tilde{f}^{LM}_{nl_1l_2} \sim \frac{1}{k_{n_0}} \sin\left(k_{n_0} r - \frac{l_2^0 \pi}{2}\right) C^{LM}_{l_1^0\mu_1^0 l_2^0 0}\, \delta_{nn_0} +$$

$$+ \sum_{\mu_1,\mu_2} q^{l_2^0\mu_2^0 l_2\mu_2}_{n_0 l_1^0\mu_1^0 nl_1\mu_1} C^{LM}_{l_1\mu_1l_2\mu_2} \frac{e^{i\left(k_n r - \frac{l_2\pi}{2}\right)}}{r} \tag{11.8}$$

We now divide both parts of (11.8) by $C^{LM}_{l_1^0\mu_1^0 l_2^0 0}$ and substitute

$$f^{LM}_{nl_1l_2} = \frac{1}{C_{l_1^0\mu_1^0 l_2^0 0}} \tilde{f}^{LM}_{nl_1l_2} \tag{11.9}$$

On the total angular-momentum representation the function $f^{LM}_{n_1l_1l_2}$ has the standard asymptotic form

$$f^{LM}_{nl_1l_2} \sim \frac{1}{k_{n_0}} \sin\left(k_{n_0} r - \frac{l_2^0 \pi}{2}\right) \delta_{nn_0}\delta_{l_1l_0} + q^{LM}_{n_0 l_1^0 l_2^0 nl_1l_2} \frac{e^{i\left(k_n r - \frac{l_2\pi}{2}\right)}}{r} \tag{11.10}$$

where

$$q^{LM}_{n_0 l_1^0 l_2^0 nl_1l_2} C^{LM}_{l_1^0\mu_1^0 l_2^0 0} = \sum_{\mu_1,\mu_2} C^{LM}_{l_1\mu_1l_2\mu_2} q^{l_2^0\mu_2^0 l_2\mu_2}_{n_0 l_1^0\mu_1^0 nl_1\mu_1} \tag{11.11}$$

Using the orthogonality of the Clebsch-Gordon coefficients

$$\sum_L C^{LM}_{l_1\mu_1l_2\mu_2} C^{LM}_{l_1'\mu_1'l_2'\mu_2'} = \delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{\mu_1\mu_1'}\delta_{\mu_2\mu_2'} \tag{11.12}$$

we can solve equation (11.11) to yield

$$q^{l_2^0\mu_2^0 l_1\mu_1}_{n_0 l_1^0\mu_1^0 nl_1\mu_1} = \sum_L C^{LM}_{l_1^0\mu_1^0 l_2^0 0}\, q^{LM}_{n_0 l_1^0 l_2^0 nl_1l_2} C^{LM}_{l_1\mu_1l_2\mu_2} \tag{11.13}$$

Consider now the transformation of the matrix elements $\mathscr{V}^{l_2\mu_2l_2'\mu_2'}_{nl_1\mu_1n'l_1'\mu_1'}$ and $\mathscr{W}^{l_2\mu_2l_2'\mu_2'}_{nl_1\mu_1n'l_1'\mu_1'}$. In accordance with the general formulae for the transformation of matrices

$$A^{LM}_{l_1l_2l_1'l_2'} = \sum_{\mu_1\mu_2\mu_1'\mu_2'} C^{LM}_{l_1\mu_1l_2\mu_2} C^{LM}_{l_1'\mu_1'l_2'\mu_2'} A^{l_2\mu_2l_2'\mu_2'}_{l_1\mu_1l_1'\mu_1'} \tag{11.14}$$

Commencing with $\mathscr{V}$, we have, using the definition (10.20),

$$V_{\alpha\alpha'}(r) = -\frac{1}{r}\delta_{nn'}\delta_{l_1l_1'} + \left(\frac{1}{|r-r'|}\right)_{nl_1\mu_1n'l_1'\mu_1'} \tag{11.15}$$

We expand $|r-r'|^{-1}$ in terms of the Legendre polynomials

$$|r-r'|^{-1} = \sum_{\lambda=0}^{\infty} \gamma_\lambda(r,r') P_\lambda(\cos\omega) \tag{11.16}$$

where $\omega$ is the angle between $r$ and $r'$ and

$$\gamma_\lambda(r,r') = \begin{cases} \dfrac{r'^\lambda}{r^{\lambda+1}} & r \geqslant r' \\[2ex] \dfrac{r^\lambda}{r'^{\lambda+1}} & r' \geqslant r \end{cases} \tag{11.17}$$

We then have

$$V_{\alpha\alpha'}(r) = -\frac{1}{r}\delta_{nn'}\delta_{l_1l_1'} + \sum_\lambda (\gamma_\lambda)_{nl_1n'l_1'} \int Y^*_{l_1\mu_1}(\theta',\varphi') P_\lambda(\cos\omega) Y_{l_1'\mu_1'}(\theta',\varphi')\, d\Omega' \tag{11.18}$$

where

$$(\gamma_\lambda)_{nl_1n'l_1'} = \int_0^\infty R_{nl_1}(r')\gamma_\lambda(r,r') R_{n'l_1'}(r') r'^2\, dr' \tag{11.19}$$

($R_{nl_1}$ and $R_{n'l_1'}$ are the radial wave functions for the atomic electron.) Substitution of (11.18) into (11.4) yields

$$\begin{aligned} \mathscr{V}^{l_2\mu_2l_2'\mu_2'}_{nl_1\mu_1n'l_1'\mu_1'} = &-\frac{1}{r}\delta_{nn'}\delta_{l_1l_1'} + \\ &+ \sum_\lambda (\gamma_\lambda)_{nl_1n'l_1'} \int Y^*_{l_2\mu_2}(\theta,\varphi) Y_{l_2'\mu_2'}(\theta,\varphi) P_\lambda(\cos\omega) Y^*_{l_1\mu_1}(\theta',\varphi') \\ &\times Y_{l'_1\mu'_1}(\theta',\varphi')\, d\Omega\, d\Omega' \end{aligned} \tag{11.20}$$

We now use the transformation (11.14), for simplicity denoting by $\nu$ the group of indices

$$\nu = nl_1 l_2$$

As a result we obtain

$$\begin{aligned} \mathscr{V}^{LM}_{\nu\nu'} = &-\frac{1}{r}\delta_{\nu\nu'} + \sum_\lambda (\gamma_\lambda)_{nl_1n'l_1'} \sum_{\mu_1\mu_1'\mu_2\mu_2'} C^{LM}_{l_1\mu_1l_2\mu_2} C^{LM}_{l_1'\mu_1'l_2'\mu_2'} \\ &\times \int Y^*_{l_2\mu_2}(\theta,\varphi) Y_{l_2'\mu_2'}(\theta,\varphi) P_\lambda(\cos\omega) Y^*_{l_1\mu_1}(\theta',\varphi') \\ &\times Y_{l_1'\mu_1'}(\theta',\varphi')\, d\Omega\, d\Omega' \end{aligned} \tag{11.21}$$

The expression

$$h_\lambda = \sum_{\mu_1\mu_2\mu_1'\mu_2'} C^{LM}_{l_1\mu_1 l_2\mu_2} C^{LM}_{l_1'\mu_1' l_2'\mu_2'} \int Y^*_{l_2\mu_2}(\theta, \varphi) Y_{l_2'\mu_2'}(\theta, \varphi) P_\lambda(\cos\omega) Y^*_{l_1\mu_1}(\theta', \varphi') \times Y_{l_1'\mu_1'}(\theta', \varphi')\, d\Omega\, d\Omega' \quad (11.22)$$

which enters into (11.21) is independent of $M$ and can be expressed in terms of the Racah coefficient $w$:

$$h_\lambda(l_1, l_2, l_1', l_2', L) = (-1)^{l_1'+l_1-L}(2\lambda+1)^{-1} w(l_1, l_1', l_2, l_2', \lambda) \times C^{\lambda 0}_{l_1 0 l_1' 0} C^{\lambda}_{l_2 0 l_2' 0}(2l_1+1)^{\frac{1}{2}}(2l_1'+1)^{\frac{1}{2}}(2l_2+1)^{\frac{1}{2}}(2l_2'+1)^{\frac{1}{2}} \quad (11.23)$$

Therefore,

$$\mathscr{V}^L_{vv'}(r) = -\frac{1}{r}\delta_{vv'} + \sum_\lambda (\gamma_\lambda)_{nl_1 n' l_1'} h_\lambda(l_1, l_2, l_1', l_2', L) \quad (11.24)$$

For large $r$ we have

$$\gamma_\lambda \sim r^{-\lambda-1}$$

so that (11.24) is a multipole expansion of $\mathscr{V}^L_{vv'}$. The quantity $h_\lambda$ has a non-zero value only under the following conditions:

(1) The triads $l_1$, $l_2$, $L$ and $l_1'$, $l_2'$, $L$ satisfy the usual rules for the combination of angular momenta.

(2) $l_1$, $l_2$ and $l_1'$, $l_2'$ satisfy the condition expressing the conservation of parity, i.e.

$$(-1)^{l_1+l_2} = (-1)^{l_1'+l_2'} \quad (11.25)$$

(3) The parameter $\lambda$ satisfies the inequalities

$$\begin{aligned} |l_1 - l_1'| &\leqslant \lambda \leqslant (l_1 + l_1') \\ |l_2 - l_2'| &\leqslant \lambda \leqslant (l_2 + l_2') \end{aligned} \quad (11.26)$$

which follow from the properties of $C^{\lambda 0}_{l_1 0 l_1' 0}$ and $C^{\lambda 0}_{l_2 0 l_2' 0}$; when $\lambda = 0$

$$h_0 = \delta_{l_1 l_1'} \delta_{l_2 l_2'} \quad (11.27)$$

The quantity $h$ is tabulated in [28] for certain values of $l_1$, $l_2$, $l_1'$, $l_2'$, and $\lambda$.

We can transform $\mathscr{W}$ in a similar way. Starting with (10.52) and using (10.60) we obtain the following result

$$\mathscr{W}^L_{vv'}(r', r) = \pm \sum_\lambda g_\lambda(l_1, l_2, l_1', l_2', L) \times [\delta_{\lambda 0}(E_0 - \tfrac{1}{2}k_v^2) + \gamma_\lambda(r', r)] R_{nl_1}(r) R_{n'l_1'}(r') \quad (11.28)$$

where

$$g_\lambda(l_1, l_2, l_1', l_2', L) = (-1)^{l_1'-l_2'}(2\lambda+1)^{-1} w(l_1, l_2, l_2', l_1', \lambda) \times C^{\lambda 0}_{l_1 0 l_2' 0} C^{\lambda 0}_{l_2 0 l_1' 0}(2l_1+1)^{\frac{1}{2}}(2l_2+1)^{\frac{1}{2}}(2l_1'+1)^{\frac{1}{2}}(2l_2'+1)^{\frac{1}{2}} \quad (11.29)$$

and $g_\lambda \neq 0$ when

$$|l_1 - l_2'| \leqslant \lambda \leqslant (l_1 + l_2'); \qquad |l_2 - l_1'| \leqslant \lambda \leqslant (l_2 + l_1')$$

The quantity $g_\lambda$ is also tabulated in [28].

It follows from (11.17) that when $r < r'$

$$\mathscr{W}^{(1)L}_{vv'}(r',r) = \pm \sum_{\lambda} g_{\lambda} \left[\delta_{0\lambda}\left(E_{v'} - \frac{k_v^2}{2}\right) + \frac{r^{\lambda}}{r'^{\lambda+1}}\right] R_{nl_1}(r') R_{n'l_1'}(r) \qquad (11.30)$$

whilst when $r \geqslant r'$

$$\mathscr{W}^{(2)L}_{vv'}(r',r) = \pm \sum_{\lambda} g_{\lambda} \left[\delta_{0\lambda}(E_{v'} - \tfrac{1}{2}k_v^2) + \frac{r'^{\lambda+1}}{r^{\lambda}}\right] R_{nl_1}(r') R_{n'l_1'}(r) \qquad (11.31)$$

On the total angular momentum representation, the integro-differential equations (11.6) for the partial waves assume the form

$$\frac{d^2 f_v^L}{dr^2} + \left[k_0^2 - \frac{l_2(l_2+1)}{r^2}\right] f_v^L = 2 \sum_{v'} \left[\mathscr{V}^L_{vv'}(r) f^L_{v'}(r) + \int_0^{\infty} \mathscr{W}^L_{vv'}(r',r) f^L_{v'}(r')\, dr'\right] \qquad (11.32)$$

Henceforward we shall omit the superscript $L$ whenever this leads to ambiguities.

The possible values of $l_2$ for different $n_1$, $l_1$ and $L$ are given in Table 1 for $(-1)^{l_1+l_2} = (-1)^L$ and in Table 2 for $(-1)^{l_1+l_2} = (-1)^{L-1}$.

TABLE 1

| | $n_1$; $l_1$ | | | | | |
|---|---|---|---|---|---|---|
| $L$ | 1; 0 | 2; 0 | 2; 1 | 3; 0 | 3; 1 | 3; 2 |
| 0 | 0 | 0 | 1 | 0 | 1 | 2 |
| 1 | 1 | 1 | 0; 2 | 1 | 0; 2 | 1; 3 |
| 2 | 2 | 2 | 1; 3 | 2 | 1; 3 | 0; 2; 4 |
| 3 | 3 | 3 | 2; 4 | 3 | 2; 4 | 1; 3; 5 |

TABLE 2

| | $n_1$; $l_1$ | |
|---|---|---|
| $L$ | 2; 1 | 3; 1 |
| 0 | | |
| 1 | 1 | 1 |
| 2 | 2 | 2 |
| 3 | 1; 3 | 1; 3 |

The system of integro-differential equations (11.32) can be transformed into a system of integral equations:

$$f_v = c_{v_0 v} u_v(r) + \sum_{v'} \int_0^{r} M_{vv'}(r,r') f_{v'}(r')\, dr' + \sum_{v'} \int_0^{\infty} N_{vv'}(r,r') f_{v'}(r')\, dr' \qquad (11.33)$$

where $c_{\nu_0\nu}$, $M_{\nu\nu'}$ and $N_{\nu\nu'}$ are defined by

$$M_{\nu\nu'}(r,r') = 2[v_\nu(r)u_\nu(r')-v_\nu(r')u_\nu(r)]\mathcal{V}_{\nu\nu'}(r') + 2\int_{r'}^{r}[v_\nu(r)u_\nu(r'')-v_\nu(r'')u_\nu(r)] \times[\mathcal{W}^{(1)}_{\nu\nu'}(r'',r')-\mathcal{W}^{(2)}_{\nu\nu'}(r'',r')]\,dr'' \qquad (11.34)$$

$$N_{\nu\nu'}(r,r') = 2\int_0^r [v_\nu(r)u_\nu(r'')-v_\nu(r'')u_\nu(r)]\mathcal{W}^{(2)}_{\nu\nu'}(r'',r')\,dr'' \qquad (11.35)$$

$$c_{\nu_0\nu} = \delta_{\nu_0\nu}+2\sum_{\nu'}\int_0^\infty\left[v_\nu(r')\mathcal{V}_{\nu\nu'}(r')+\int_0^\infty \mathcal{W}_{\nu\nu'}(r'',r')v_\nu(r'')\,dr''\right]f_{\nu'}(r')\,dr' \qquad (11.36)$$

$$\left.\begin{aligned} u_\nu(r) &= \sqrt{\frac{\pi r}{2k_\nu}}J_{l+\frac{1}{2}}(k_\nu,r)\\ v_\nu(r) &= -i\sqrt{\frac{\pi k_\nu r}{2}}H^{(1)}_{l+\frac{1}{2}}(k_\nu,r)\end{aligned}\right. \qquad (11.37)$$

The integral equation for the partial amplitude is of the form

$$q_{\nu_0\nu} = -2\sum_{\nu'}\int_0^\infty\left[u_\nu(r')\mathcal{V}_{\nu\nu'}(r')+\int_0^\infty u_\nu(r'')\mathcal{W}_{\nu\nu'}(r'',r')\,dr''\right]f_{\nu'}(r')\,dr' \qquad (11.38)$$

We can carry out a transformation on (11.33), analogous to (2.39). In particular, we can introduce new functions $x_{\nu\nu'}$ which are related to $f_\nu$ by

$$f_\nu(r) = \sum_{\nu'} c_{\nu_0\nu'}x_{\nu\nu'}(r) \qquad (11.39)$$

We then have

$$x_{\nu\nu''} = u_\nu\delta_{\nu\nu''} + \sum_{\nu'}\int_0^r M_{\nu\nu'}x_{\nu'\nu''}\,dr' + \sum_{\nu'}\int_0^\infty N_{\nu\nu'}x_{\nu'\nu''}\,dr' \qquad (11.40)$$

From equation (11.36) are obtained the following equations for $c_{\nu_0\nu}$:

$$c_{\nu_0\nu} = \delta_{\nu_0\nu}+2\sum_{\nu'\nu''}c_{\nu_0\nu'}\int_0^\infty\left[v_\nu(r')\mathcal{V}_{\nu\nu'}(r')+\int_0^\infty v_\nu(r'')\mathcal{W}_{\nu\nu'}(r'',r')\,dr'\right]x_{\nu'\nu''}(r')\,dr' \qquad (11.41)$$

On substituting (11.39) into (11.38), we obtain an expression for $q_{\nu_0\nu}$ in terms of the functions $x_{\nu\nu'}$:

$$q_{\nu_0\nu} = -2\sum_{\nu'\nu''}c_{\nu_0\nu''}\int_0^\infty\left[u_\nu(r')\mathcal{V}_{\nu\nu'}(r')+\int_0^\infty u_\nu(r'')\mathcal{W}_{\nu\nu'}(r'',r')\,dr''\right]x_{\nu'\nu''}(r')\,dr' \qquad (11.42)$$

Let

$$L_{\nu''\nu} = \delta_{\nu''\nu}-2\sum_{\nu'}\int_0^\infty\left[v_\nu(r')\mathcal{V}_{\nu\nu'}(r')+\int_0^\infty \mathcal{W}_{\nu\nu'}(r'',r')v_\nu(r'')\,dr''\right]x_{\nu'\nu''}(r')\,dr' \qquad (11.43)$$

The matrix $L_{\nu'\nu}$ is a generalization of the Jost function given by (2.41).

We can use the properties of Bessel functions to write the matrix element $L_{\nu''\nu}$ in the form

$$L_{\nu''\nu} = k_{\nu''}^{l_2''} A_{\nu''\nu} k_\nu^{-l_2} + i k_{\nu''}^{l_2''} B_{\nu''\nu} k_\nu^{l_2+1} \tag{11.44}$$

where

$$A_{\nu''\nu} = \delta_{\nu''\nu} + 2(-1)^{l_2} k_{\nu''}^{-l_2''} k_\nu^{l_2+1} \sum_{\nu'} \int_0^\infty \left( u_{-l_2-1} \mathscr{V}_{\nu\nu'} + \int_0^\infty \mathscr{W}_{\nu\nu'} u_{-l_2-l}\, dr'' \right) x_{\nu'\nu''}\, dr' \tag{11.45}$$

$$B_{\nu''\nu} = 2 k_\nu^{-l_2} k_{\nu''}^{-l_2'} \sum_{\nu'} \int_0^\infty \left( u_{l_2} \mathscr{V}_{\nu\nu'} + \int_0^\infty \mathscr{W}_{\nu\nu'} u_{l_2}\, dr'' \right) x_{\nu'\nu''}\, dr' \tag{11.46}$$

The quantities $A_{\nu''\nu}$ and $B_{\nu''\nu}$ are functions of $k_\nu^2$ and $k_{\nu''}^2$. Use can be made of (9.32), which represents the conservation of energy, to express all the $k_\nu^2$ in terms of $k_0^2$. The diagonal elements are of a form analogous to (2.45):

$$L_{\nu\nu} = A_{\nu\nu} + i k_\nu^{2l_2+1} B_{\nu\nu} \tag{11.47}$$

The system given by equation (11.41) may be written in the form

$$\sum_{\nu''} c_{\nu_0\nu''} L_{\nu''\nu} = \delta_{\nu_0\nu} \tag{11.48}$$

and the integral expression (11.42) in the form

$$q_{\nu_0\nu} = -\sum_{\nu''} c_{\nu_0\nu''} k_\nu^{l_2} k_{\nu''}^{l_2''} B_{\nu''\nu} \tag{11.49}$$

In (11.48) the summation is carried out over all the states $\nu''$, whereas in (11.49) it is carried out only over those states which are consistent with the conservation of energy. If we neglect virtual transitions and retain in (11.48) only those states over which the summation is carried out in (11.49), the number of constants in (11.48) and (11.49) will be the same.

If we consider all the possible values of $\nu_0$, the quantities $c_{\nu_0\nu}$ will form a matrix, which we denote by c. Equation (11.48) can then be written in the matrix form

$$\mathrm{cL} = 1 \tag{11.50}$$

As with $c_{\nu_0\nu}$, the amplitudes $q_{\nu_0\nu}$ depend on the subscript $\nu_0$ and form the matrix $q_{\nu_0\nu}$. Let us introduce the matrix k whose elements are $k_\nu \delta_{\nu\nu'}$. With its aid the expression (11.49) may be written in the form

$$\mathrm{q} = -\mathrm{c}\mathrm{k}^l \mathrm{B} \mathrm{k}^l \tag{11.51}$$

Substituting $\mathrm{c} = \mathrm{L}^{-1}$, we have

$$\mathrm{q} = -\mathrm{L}^{-1} \mathrm{k}^l \mathrm{B} \mathrm{k}^l \tag{11.52}$$

This is a generalization of (2.47) which expresses the scattering amplitude in terms of the Jost function.

From the unitary relationships (10.60) we can obtain the corresponding relationship for the partial amplitudes. When the atom is in the ground state prior to collision we have

$$\operatorname{Im} q_{00}^L - k_0 |q_{00}^L|^2 = \sum_{\nu \neq 0} k_\nu |q_{0\nu}^L|^2 \tag{11.53}$$

and $l_1^0 = 0$, $l_2^0 = L$.

If the energy of the incident electron is too low for excitation to occur, the sum on the right-hand side will vanish and we return to (2.29). Let

$$q_{00}^{L} = \frac{\beta_L - 1}{2ik_0} \tag{11.54}$$

The partial cross-section for elastic scattering is then

$$\sigma_{00} = (2L+1)\frac{\pi}{k_0^2}|\beta_L - 1|^2 \tag{11.55}$$

and the partial cross-section for all the inelastic processes is

$$\sum_{\nu \neq 0} \sigma_{0\nu}^{L} = (2L+1)\frac{\pi}{k_0^2}(1 - |\beta_L|^2) \tag{11.56}$$

which follows from (11.12). Hence the partial cross-section for all the inelastic processes is at all times smaller than $\pi(2L+1)/k_0^2$.

## 12. Elastic and Inelastic Scattering Cross-sections. Behaviour Near the Threshold

Let us now return to the general properties of the amplitudes. To begin with, we shall transform (11.52) to a more convenient form, using (11.44). In matrix notation, the latter expression is of the form

$$\mathrm{L} = \mathrm{k}^{l}\mathrm{A}\mathrm{k}^{-l} + i\mathrm{k}^{l}\mathrm{B}k^{l+1} \tag{12.1}$$

Substituting

$$\mathrm{A} = -\mathrm{B}\mathrm{M} \tag{12.2}$$

into (12.1), we have

$$\mathrm{L} = -\mathrm{k}^{l}\mathrm{B}(\mathrm{M}\mathrm{k}^{-l} - i\mathrm{k}^{l+1}) \tag{12.3}$$

Using (11.52) together with the latter expression, we obtain

$$\mathrm{q} = [\mathrm{k}^{l}\mathrm{B}(\mathrm{M}\mathrm{k}^{-l} - i\mathrm{k}^{l+1})]^{-1}\mathrm{k}^{l}\mathrm{B}\mathrm{k}^{l} \tag{12.4}$$

or

$$\mathrm{q} = (\mathrm{M}\mathrm{k}^{-l} - i\mathrm{k}^{l+1})^{-1}\mathrm{B}^{-1}\mathrm{k}^{-l}\mathrm{k}^{l}\mathrm{B}\mathrm{k}^{l}$$

and hence finally

$$\mathrm{q} = \mathrm{k}^{l}(\mathrm{M} - i\mathrm{k}^{2l+1})^{-1}\mathrm{k}^{l} \tag{12.5}$$

Bearing in mind (10.57), we obtain the following expression for the T-matrix

$$(2\pi)^2\mathrm{T} = \mathrm{k}^{l+\frac{1}{2}}(\mathrm{M} - i\mathrm{k}^{2l+1})^{-1}\mathrm{k}^{l+\frac{1}{2}} \tag{12.6}$$

This representation of the T-matrix is used in the general theory of multichannel processes [29]. It is evident from the preceding discussion that this representation is a natural consequence of the properties of the Jost matrix. The formula (12.2) establishes the relation between the M-matrix and the Jost matrix. The matrix M is real and symmetric, which ensures that

$$\mathrm{T}^{+} - \mathrm{T} = 2\pi i\mathrm{T}\mathrm{T}^{+} \tag{12.7}$$

We recall one further representation [30] also used in the theory of multichannel processes involving the so-called reaction matrix K, which is given in terms of M by the expression

$$\mathrm{M} = \mathrm{k}^{l+\frac{1}{2}}\mathrm{K}^{-1}\mathrm{k}^{l+\frac{1}{2}} \tag{12.8}$$

The amplitude q is

$$\mathrm{q} = \mathrm{k}^{-\frac{1}{2}}\mathrm{K}(1-i\mathrm{K})^{-1}\mathrm{k}^{-\frac{1}{2}} \tag{12.9}$$

and the T-matrix

$$(2\pi)^2\mathrm{T} = \mathrm{K}(1-i\mathrm{K})^{-1} \tag{12.10}$$

It follows from (12.2) and (12.5) that the reaction matrix

$$\mathrm{K} = -\mathrm{k}^{l+\frac{1}{2}}\mathrm{B}\mathrm{A}^{-1}\mathrm{k}^{l+\frac{1}{2}} \tag{12.11}$$

The expression (12.5) is convenient for the investigation of the dependence of the cross-section on energy, particularly near the excitation threshold.

As an example, consider a simple two-channel system [29] and suppose that the incident particle is in the $s$-state both before and after the collision. In spite of the fact that this is a much simplified example, it does exhibit certain general features characteristic of real multi-channel systems.

By (12.5) the elements of the matrix q are of the form

$$q_{11} = \frac{M_{22}-ik_2}{D} \tag{12.12}$$

$$q_{12} = q_{21} = \frac{M_{12}}{D} \tag{12.13}$$

$$q_{22} = \frac{M_{11}-ik_1}{D} \tag{12.14}$$

where

$$D = (M_{11}-ik_1)(M_{22}-ik_2)-M_{12}^2 \tag{12.15}$$

$$k_2 = \sqrt{k_1^2-2\Delta E} \tag{12.16}$$

and $\Delta E$ is the excitation threshold. Below the threshold let

$$k_2 = i\kappa = i\sqrt{2\Delta E-k_1^2} \tag{12.17}$$

The effective cross-sections are then given by

$$\sigma_{ik} = 4\pi\frac{k_k}{k_i}|q_{ik}|^2 \qquad i, k = 1, 2 \tag{12.18}$$

When the energy of the incident particle lies above the threshold, i.e. when $E_1 = \frac{1}{2}k_1^2 > \Delta E$, the scattering and excitation cross-sections are respectively

$$\sigma_{11} = 4\pi\frac{M_{22}^2+k_2^2}{(M_{11}M_{22}-M_{12}^2-k_1k_2)^2+(k_1M_{22}+k_2M_{11})^2} \tag{12.19}$$

$$\sigma_{12} = 4\pi\frac{k_2}{k_1}\frac{M_{12}^2}{(M_{11}M_{22}-M_{12}^2-k_1k_2)^2+(k_1M_{22}+k_2M_{11})^2} \tag{12.20}$$

When the energy of the incident particle lies below the threshold, i.e. when $E_1 < \Delta E$, we have

$$\sigma_{11} = 4\pi \frac{(M_{22}+\kappa)^2}{[M_{11}(M_{22}+\kappa)-M_{12}^2]^2+k_1^2(M_{22}+\kappa)^2} \tag{12.21}$$

which can also be written in the form

$$\sigma_{11} = \frac{4\pi}{k_1^2}\sin^2\delta \tag{12.22}$$

where

$$\sin^2\delta = \frac{k_1^2(M_{22}+\kappa)^2}{[M_{11}(M_{22}+\kappa)-M_{12}^2]^2+k_1^2(M_{22}+\kappa)^2} \tag{12.23}$$

Consider the behaviour of the cross-sections near threshold.

To within linear terms in $k_2$ in the amplitudes $|q_{i,k}|$ we have above the threshold

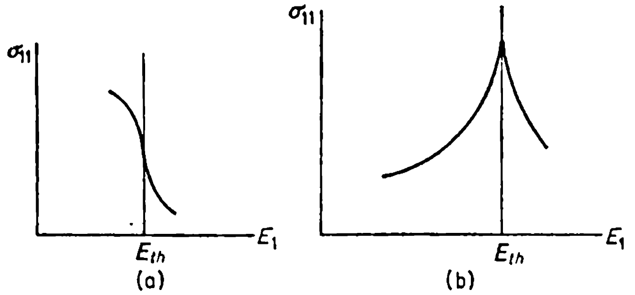
$$\sigma_{11} = 4\pi|q_{11}^{(0)}|^2(1-2k_1^{(0)}k_2|q_{12}^{(0)}|^2) \tag{12.24}$$

$$\sigma_{12} = 4\pi\frac{k_2|q_{12}^{(0)}|^2}{k_1^{(0)}}(1-2k_1^{(0)}k_2|q_{12}^{(0)}|^2) \tag{12.25}$$

where the superscript 0 indicates that the particular quantity is taken where $k_2 = 0$, i.e. at threshold.

Below threshold

$$\sigma_{11} = 4\pi|q_{11}^{(0)}|^2(1-2k_1^{(0)}|q_{12}^{(0)}|^2\kappa\cot\delta^{(0)}) \tag{12.26}$$



(a) (b)

FIG. 7. Elastic scattering cross-sections near the excitation threshold: (*a*) cot $\delta < 0$, (*b*) cot $\delta > 0$ ($E_{th}$ is the threshold energy)

Comparison of equations (12.24) and (12.26) shows that $d\sigma_{11}/dE_1$ has a singularity at threshold.† At energies above threshold, $\sigma_{11}$ decreases with increasing $E_1$, and the character of the variation depends on the sign of cot $\delta^{(0)}$ below threshold. If cot $\delta^{(0)} > 0$, $\sigma_{11}$ decreases with decreasing $E_1$. But, if cot $\delta^{(0)} < 0$, $\sigma_{11}$ increases with decreasing $E_1$.

The variation of $\sigma_{11}$ with $E_1$ is illustrated in Fig. 7. Apart from the singularity at threshold, the cross-section $\sigma_{11}$ can also exhibit a resonance maximum in the sub-threshold region. As can be seen from equations (12.22) and (12.23), the maximum will occur when $\sin^2 \delta = 1$, i.e. when

---

† Elastic scattering at the threshold for inelastic scattering has been investigated by many authors (see, for example, [31, 32]).

$$M_{11}(M_{22}+\kappa)-M_{12}^2 = 0 \tag{12.27}$$

The width of the resonance peak depends on the ratio $M_{11}/M_{12}$. It can be shown [29] that the peak is sharp when $|M_{11}/M_{12}| \gg 1$.

Figure 8 shows a typical variation of $\sigma$ with $E$ for the two kinds of threshold singularity and in the presence of resonance.

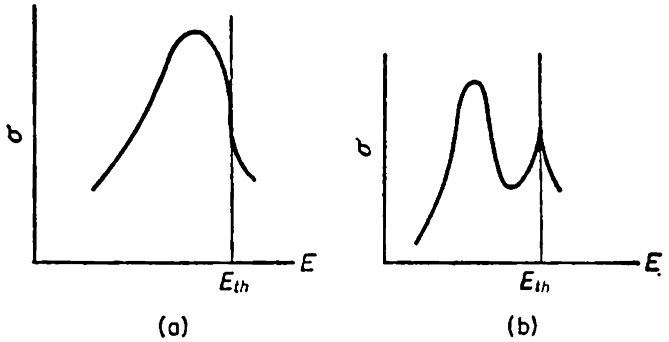


FIG. 8. Elastic scattering resonance near the excitation threshold: (*a*) $\cot \delta < 0$, (*b*) $\cot \delta > 0$

Numerical calculations carried out for a potential well [29] show that for some values of the parameters one does in fact obtain resonance peaks near the threshold.

Equations (12.24)–(12.26) are valid in the immediate neighbourhood of the threshold. It is possible to obtain approximate formulae which hold in a broader region by retaining in the amplitudes $q_{ik}$ terms which are quadratic in $k_2$. With this intention, the quantities $A_{ik}$ and $B_{ik}$ in the Jost matrix (12.1) are expanded in powers of $k_2^2$. An approximate formula for $\sigma_{12}$ has been obtained [33] in this way. A basically similar approach is used in [29], where the matrix $M_{ik}$ is expanded in powers of $k_2^2$. Calculating $\sigma_{11}$ by means of equation (12.21), in which the matrix elements $M_{ik}$ are represented by the two-term expansion

$$M_{ik}(\kappa) = M_{ik}(0)+R_{ik}\kappa^2 \tag{12.28}$$

it is possible to carry out an approximate study of the behaviour of $\sigma$ near resonance. This method is used in [34] to investigate the resonance in the elastic cross-section of the hydrogen atom for electron scattering, assuming a single excitation channel (excitation of the 2*s*-state).

If the angular momentum of the particle after collision has a non-zero value and is equal to, say, $l$, then according to (12.5) the excitation amplitude $q_{12}$ near the threshold varies as $k_2^l$. The excitation cross-section near the threshold is

$$\sigma_{12} \sim k_2^{2l+1} \tag{12.29}$$

The elastic scattering cross-section at the threshold will then no longer have a singularity of the form shown in Fig. 7*a* or 7*b* since $d\sigma_{11}/dE$ is continuous at the threshold.

The resonance in $\sigma_{11}$ below the threshold can also exist when $l \neq 0$. In the presence of three or more connected channels, the resonances can appear not only in the elastic scattering cross-section but also in the inelastic cross-section between two neighbouring thresholds.

The case when there is degeneracy, i.e. two or more channels at the same energy, occupies a special position. It is encountered in collisions with hydrogen atoms. Since the matrix elements $V_{\nu\nu'}$ include elements which fall off as $r^{-2}$ as $r \to \infty$, the behaviour of $\sigma$ near the threshold will be different from that indicated by equation (12.29) [35].

*Chapter 4*

# THE ELASTIC SCATTERING OF AN ELECTRON BY A HYDROGEN ATOM

## 13. THE SCATTERING OF AN ELECTRON BY A HYDROGEN ATOM REGARDED AS A CENTRE OF FORCE

As has already been pointed out, the elastic scattering of an electron by an atom can be described in various approximate ways as the superposition of three effects: the central-force interaction between the electron and the nucleus, the exchange interaction, and polarization of the atom by the electric field of the incident electron. All these effects are allowed for formally in the exact equations for the function $F_0$. If we take for $F_\alpha$ the system of equations (10.55), the terms $V_{00}F_0$ and $\int W_{00}F_0\,dr$ represent the central-force and exchange interactions between the electron and the atom in the ground state, while the sum

$$\sum_\alpha \left(V_{0\alpha}F_\alpha + \int W_{0\alpha}F_\alpha dr\right)$$

represents the effect of polarization and the connection between the elastic and inelastic processes. By neglecting one of the factors it is possible to obtain simple equations which admit of a practical solution. Furthermore, the relative importance of the various factors may be estimated by comparing the results of different approximate calculations.

The crudest approximation involves the rejection in the equation for $F_0$ of all the terms containing $F_\alpha$ and the term describing the exchange interaction. In that case the system of equations reduces to a single equation. For simplicity, we shall omit the subscripts so that the equation for $F_0$ becomes

$$\Delta F+(k^2-2V)F = 0 \tag{13.1}$$

According to equation (10.20),

$$V(r) = -\frac{1}{r}+\int\frac{|\psi_0(r')|^2}{|r-r'|}dr'$$

Substituting the expression for the wave function of the hydrogen atom in the ground state

$$\psi_0 = \frac{1}{\sqrt{\pi}}e^{-r}$$

and completing the integration, we have

$$V(r) = -e^{-2r}\left(1+\frac{1}{r}\right) \tag{13.2}$$

The asymptotic expression for $F_\alpha$ is

$$F \approx e^{ik\mathbf{v}.\mathbf{r}} + q\frac{e^{ikr}}{r} \tag{13.3}$$

This approximation is equivalent to assuming that the atom behaves as a centre of force.

On separating the angular variables

$$f_l'' + \left[k^2 - \frac{l(l+1)}{r^2} - 2V\right] f_l = 0 \tag{13.4}$$

for which the systematic solution is

$$f_l \sim \frac{e^{i\delta_l}}{k}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right)$$

Equation (13.4) has been solved numerically for $l = 0$ and $l = 1$ for $0 \leqslant k^2 \leqslant 1{\cdot}75$ [36, 37]. According to [37], the scattering length is $a = -9{\cdot}44$. The large value of the scattering length and the negative sign indicate the presence of a virtual level near zero energy.

A reasonable approximation to the numerical calculations [36] can be obtained by the method of trial potential (§ 6). We shall take the trial expression for $V_0$ in the form†

$$V_0 = \begin{cases} \dfrac{1}{R} - \dfrac{1}{r} & r < R \\ 0 & r \geqslant R \end{cases} \tag{13.5}$$

where $R$ is determined from the condition given by equation (6.7).

For the $s$-wave at zero energy, we have

$$\begin{aligned} f_0'' - 2\left(\frac{1}{R} - \frac{1}{r}\right) f_0 &= 0 \qquad r \leqslant R \\ f_0'' &= 0 \qquad r \geqslant R \end{aligned} \tag{13.6}$$

When $r \leqslant R$, the solution given by (13.6), which satisfies the condition $f_0(0) = 0$, is

$$f_0 = Cr e^{-\sqrt{\frac{2}{R}}r} F\left(1 - \sqrt{\frac{R}{2}}, 2, 2\sqrt{\frac{2}{R}}r\right) \tag{13.7}$$

where $F$ is the degenerate hypergeometric function and $C$ is a normalizing constant. When $r \geqslant R$ the function $f_0$ is of the form

$$f_0 = r + q \tag{13.8}$$

---

† Expressions of this form were used in the 1930's to investigate certain general properties of the phase $\delta$ [38]. In this paper the parameter $R$ was determined with the aid of the semi-empirical rules of Slater for the atomic radii (developed in the theory of atomic spectra). However, the phase $\delta$ is very sensitive to changes in $R$, particularly at low energies. Therefore intuitive considerations leading merely to an order of magnitude for R are inadequate in the present context.

or on introducing the scattering length $a_0 = -q$,

$$f_0 = r - a_0 \tag{13.9}$$

The continuity condition for the function and its derivative at $r = R$ yields relations giving $C$ and $a_0$ in terms of $f_0(R)$ and $f_0'(R)$. In particular,

$$a_0 = R - \frac{f_0(R)}{f_0'(R)}$$

The parameter $R$ can be determined from equation (6.7). In the present case, this relation assumes the form

$$\int_0^R (V - V_0) f_0^2 \, dr + \int_R^\infty V f_0^2 \, dr = 0 \tag{13.10}$$

This equation has been solved numerically, and the result obtained for $R$ is

$$R = 1{\cdot}43 \tag{13.11}$$

For this value of $R$, the magnitude of $2 \int |\delta V| r \, dr$ turns out to be equal to 0·33. Therefore the condition given by (6.13) is satisfied and one can expect good agreement between wave functions calculated with $V$ and $V_0$.

The results of the calculations are as follows. The scattering length is $a = -10{\cdot}3$, quite close to the exact value of $a = -9{\cdot}44$ [37].

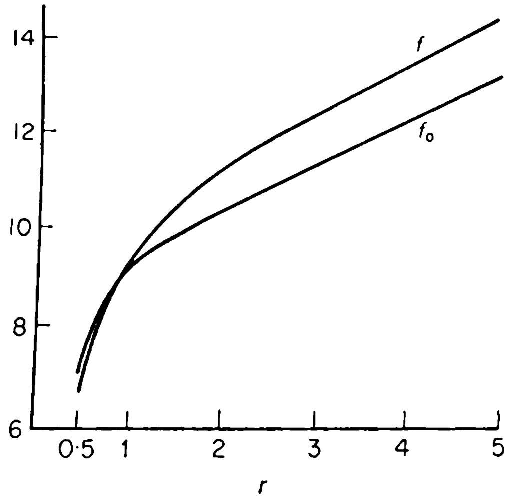


FIG. 9. The form of the functions $f_0$ and $f$ for $k = 0$

Figure 9 shows a plot of $f_0$ and a plot of the values of $f$ found in [37] by numerical integration of the equation

$$f'' - 2Vf = 0$$

In order to estimate the degree of approximation reached with the expression for $V_0$ with $k \neq 0$, consider the $s$-wave for $k \neq 0$. The corresponding equation is of the form

$$f_0'' + (k^2 - 2V_0) f_0 = 0 \tag{13.12}$$

The solution for $r < R$ is

$$_0 = cre^{-\mu r}F\left(1-\frac{1}{\mu}, 2, 2\mu r\right) \tag{13.13}$$

where

$$\mu = \sqrt{\frac{2}{R} - k^2} \tag{13.14}$$

For $r \geqslant R$ we can write the solution in the form

$$f_0 = \sin(kr+\delta_0) \tag{13.15}$$

Both the constant $c$ and $\delta_0$ can be determined by matching equations (13.13) and (13.15) at $r = R$. We note that if $\mu$ is an integer, the hypergeometric function becomes identical with the corresponding Laguerre polynomial and the calculation becomes particularly simple. For example, when

$$k^2 = \frac{2}{R} - 1 = 0{\cdot}40 \tag{13.16}$$

and $\mu = 1$, we have

$$f_0 = cre^{-r} \tag{13.17}$$

A function $f$ suitable for the comparison ($k^2 = 0{\cdot}45$) is given in [36]. Figure 10 shows the values of $f_0$ and $f$. The phases $\delta_0$ and $\delta$ are, respectively, equal to 1.11 and 1.01.

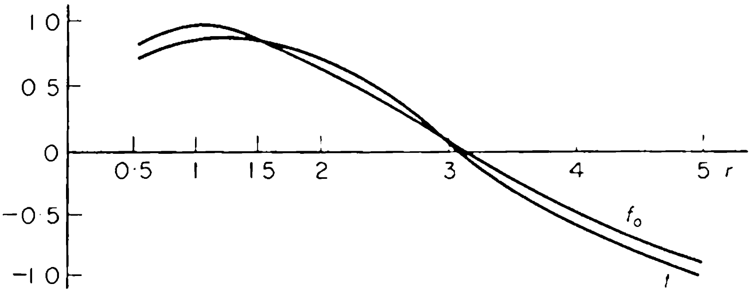


FIG. 10. The form of the functions $f_0$ and $f$ for $k^2 = 0{\cdot}40$ and $k^2 = 0{\cdot}45$ respectively

A considerable number of calculations have been carried out by the variational method.

As in the analysis considered in § 7, one constructs the functional

$$\mathscr{L}_t = \int \psi_t(r_1, r_2)(H-\mathscr{E})\psi_t(r_1, r_2)\,dr_1\,dr_2 \tag{13.18}$$

where $H$ is the energy operator for the entire electron + atom system. The trial function $\psi_t$ should contain the atomic wave function which is not varied.

The expression

$$Q = q_t - \frac{1}{2\pi}\mathscr{L}_t \tag{13.19}$$

is stationary with respect to variations in the trial function, and when the exact wave function $\psi$ is used the parameter $Q$ is equal to the scattering amplitude. If the trial function contains $n$ parameters $c$, then by Kohn's method these parameters are defined from the stationarity condition

$$\frac{\partial \mathscr{L}_t}{\partial c_i} = 0, \qquad \frac{\partial \mathscr{L}_t}{\partial q_t} = 2\pi \tag{13.20}$$

while the scattering amplitude is given by an expression analogous to (7.8):

$$q_k = q_t - \frac{1}{2\pi}\mathscr{L}_t \tag{13.21}$$

If the atom is taken as equivalent to a centre of force, the trial function is of the form

$$\psi_1(r_1, r_2) = \psi_0(r_1)F_t(r_2) \tag{13.22}$$

where $\psi_0$ is the atomic function and $F_t$ is a function describing the scattered electron and containing the varied parameters.

In order to obtain the partial scattering amplitude, $q_l$, the function $F_t$ in (13.22) must be replaced by

$$F_{tl} = Y_{l0}(\theta, \varphi)\frac{f_l(r)}{r} \tag{13.23}$$

For example, consider the variational calculation of the scattering length in [37]. Various forms of trial function were studied including the two-parameter function

$$f_t = r - a_t(1 - e^{-2r}) + br\,e^{-r} \tag{13.24}$$

The Kohn scattering length was found to be

$$a = -9{\cdot}38 \tag{13.25}$$

## 14. EXCHANGE EFFECTS

A better approximation is obtained by retaining the exchange operator on the left-hand side of equation (10.55). This leads to the following integro-differential equation for $F_0^{\pm}$:

$$\Delta F_0^{\pm} + (k^2 - 2V)F_0^{\pm} = 2\int W^{\pm}(\mathbf{r}', \mathbf{r})F_0^{\pm}(\mathbf{r}')\,d\mathbf{r}' \tag{14.1}$$

where $V$ is given by (13.2) and

$$W^{\pm}(\mathbf{r}', \mathbf{r}) = \pm\left(\frac{1}{|\mathbf{r}' - \mathbf{r}|} - \frac{1}{2} - \frac{k^2}{2}\right)\psi_0(\mathbf{r}')\psi_0(\mathbf{r}) \tag{14.2}$$

If we separate the angular variables using the notation of (11.5) and omit both the superscript $\pm$ and subscript 0, then

$$\frac{d^2 f_l}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2} - 2V_{ll}\right]f_l = 2\int_0^{\infty} \mathcal{W}_{ll}(r', r)f_l(r')\,dr' \tag{14.3}$$

where

$$\mathcal{W}_{ll}(r', r) = \pm 4rr' e^{-(r'-r)} \left[\gamma(r, r') - \frac{k^2}{2} - \frac{1}{2}\right] \tag{14.4}$$

subject to the conditions

$$\begin{aligned} f_l(0) &= 0 \\ f_l \underset{r\to\infty}{\sim} e^{i\delta_l}\frac{1}{k}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right) \end{aligned} \tag{14.5}$$

The scattering length in the triplet and singlet states is [35]

$$a_+ = 8{\cdot}058, \quad a_- = 2{\cdot}347 \tag{14.6}$$

The wave functions are substantially modified by the introduction of the exchange interaction. For example, Fig. 11 shows the functions $f^+(r)$ and

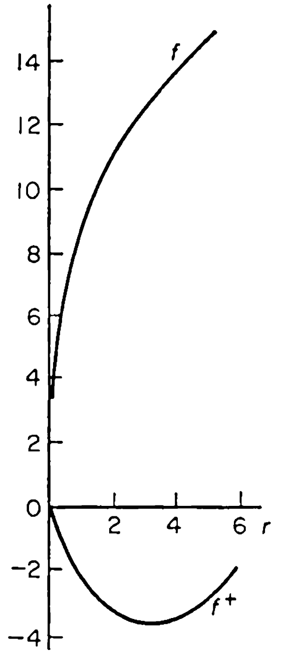


FIG. 11. The form of the functions $f^+$ and $f$ for $k = 0$

$f(r)$ for $k = 0$ in the absence of exchange. The phases $\delta_0^\pm$, $\delta_1^\pm$ and $\delta_2^\pm$ were calculated in [39] for $0 \leqslant k \leqslant 1$. The results of the calculation are illustrated in Fig. 12. Plots of $\delta_0$, $\delta_1$ and $\delta_2$ which do not include exchange effects are given for comparison. It is evident that in many cases the phase $\delta$ lies between $\delta^+$ and $\delta^-$ in the absence of exchange.

It is shown in [17] (§ 15) that in sufficiently accurate variational calculations the phase $\delta$ in the absence of exchange should tend to the half-sum $\frac{1}{2}(\delta^+ + \delta^-)$.

The numerical solution of (14.3) must be carried out by the method of successive approximations owing to the presence of the infinite integral

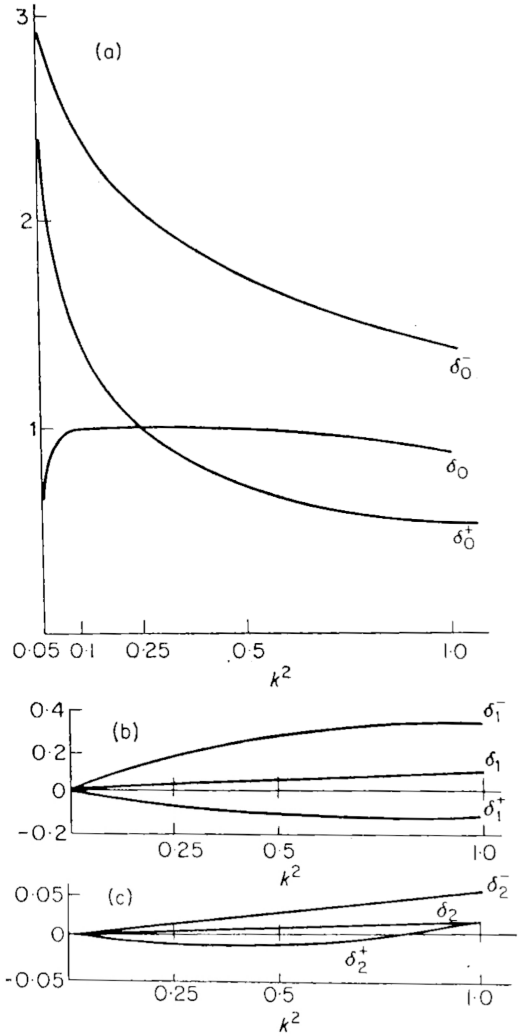


FIG. 12. The phase shifts $\delta_0{}^{\pm}$ and $\delta_0$ (*a*), $\delta_1{}^{\pm}$ and $\delta_1$ (*b*), and $\delta_2{}^{\pm}$ and $\delta_2$ (*c*)

on the right-hand side. It is shown in [39] that nine iterations are necessary. In this connection it is convenient to transform equation (14.3) to a form permitting direct solution without iteration. This transformation was carried out in [40] for the integral equation (11.35) which is equivalent to (14.3), and later by basically the same method for equation (14.3) [41].

We now consider a version of this involving the integral equation for the partial wave $l = 0$. Equation (11.33) assumes the form

$$f = C\frac{\sin kr}{k} + \int_0^r M(r,s)f(s)\,ds + \int_0^\infty N(r,s)f(s)\,ds \tag{14.7}$$

where

$$M(r,s) = \frac{2}{k}\sin k(r-s)\mathcal{V}(s) + \frac{2}{k}\int_s^r \sin k(r-t)\left[\mathcal{W}^{(1)}(s,t) - \mathcal{W}^{(2)}(s,t)\right] dt \qquad (14.8)$$

$$N(r,s) = \frac{2}{k}\int_0^r \sin k(r-t)\mathcal{W}^{(2)}(s,t)\, dt \qquad (14.9)$$

$$c = 1 - 2\int_0^\infty \left[e^{ikr}\mathcal{V}(r) + \int_0^\infty \mathcal{W}(r,s)\, e^{iks}\, ds\right] f(r)\, dr \qquad (14.10)$$

To begin with, we consider the singlet case. Let $f = cx$, so that

$$x = \frac{\sin kr}{k} + \int_0^r M(r,s)x(s)\, ds + \int_0^\infty N(r,s)x(s)\, ds \qquad (14.11)$$

$$c = \frac{1}{1 - 2\int_0^\infty \left[\mathcal{V}\, e^{ikr} + \int_0^\infty \mathcal{W}(r,s)\, e^{iks}\, ds\right] x(r)\, dr} \qquad (14.12)$$

Inspection of the expression for $N(r, s)$ given by equation (14.9) shows that it is the product of the function of $r$:

$$R(r) = \frac{8}{k}\int_0^r \sin k(r-t)\, e^{-t}\, t\, dt \qquad (14.13)$$

and the function of $s$:

$$Q(s) = s\, e^{-s}\left(\frac{2}{s} - k^2 - 1\right) \qquad (14.14)$$

i.e.

$$N = R(r)Q(s) \qquad (14.15)$$

Bearing this in mind we shall rewrite equation (14.11) in the form

$$x = \frac{\sin kr}{k} + \int_0^r Mx\, ds + R(r)c_0 \qquad (14.16)$$

$$c_0 = \int_0^\infty xQ\, ds \qquad (14.17)$$

Let

$$x = x_1 + c_0 x_0 \qquad (14.18)$$

If we substitute (14.18) into (14.16) and require that $x_1$ satisfy the equation

$$x_1 = \frac{1}{k}\sin kr + \int_0^r M(r,s)x_1(s)\, ds \qquad (14.19)$$

we have the following expression for $x_0$:

$$x_0 = R(r) + \frac{2}{k}\int_0^r M(r,s)x_0(s)\,ds \tag{14.20}$$

Equations (14.19) and (14.20) can be solved numerically without iteration. Therefore the problem formulated above is solved with the aid of transformation (14.18), which is possible because of the property indicated by (14.15). The unknown constant $c_0$ can be found in terms of $x_0$ and $x_1$. Substituting equation (14.18) into (14.17), we obtain

$$c_0 = \frac{\int_0^\infty Qx_1\,ds}{1 - \int_0^\infty Qx_0\,ds} \tag{14.21}$$

The triplet case has a specific property associated with the fact that the antisymmetric function

$$\psi(r_1, r_2) = f(r_1)\psi_0(r_2) - f(r_2)\psi_0(r_1) \tag{14.22}$$

is invariant with respect to the transformation

$$f(r_1) \to f(r_1) + \text{const}\,\psi_0(r) \tag{14.23}$$

It may be easily verified that equation (14.16) is also invariant with respect to (14.23) in the triplet case. This allows one of the two constants $c$ or $c_0$ to be chosen arbitrarily. If, for example, we set $c_0 = 0$ then

$$x = \frac{\sin kr}{k} + \int_0^r M(r,s)x(s)\,ds \tag{14.24}$$

We shall now show how to transform equation (14.3) to a form not requiring iteration.

We have

$$f'' + \left[k^2 - \frac{l(l+1)}{r^2} - 2\mathscr{V}\right] f = 2\int_0^\infty \mathscr{W}(r,s) f\,ds \tag{14.25}$$

The right-hand side of this equation may be rewritten

$$\int_0^\infty \mathscr{W} f\,ds = \int_0^r (\mathscr{W}^{(1)} - \mathscr{W}^{(2)}) f\,ds + \int_0^\infty \mathscr{W}^{(2)} f\,ds \tag{14.26}$$

Since $2\mathscr{W}^{(2)}$ may be written in the form

$$2\mathscr{W}^{(2)} = A(r)B(r') \tag{14.27}$$

we have

$$2\int_0^\infty \mathscr{W}^{(2)} f\,ds = A(r)c \tag{14.28}$$

where

$$c = \int_0^\infty Bf\,ds \tag{14.29}$$

Therefore,

$$f'' + \left[k^2 - \frac{l(l+1)}{r^2} - 2\mathcal{V}\right] f = cA(r) \tag{14.30}$$

Substituting

$$S = x + cy \tag{14.31}$$

we have two equations for $x$ and $y$ which can be solved without iteration:

$$x'' + \left[k^2 - \frac{l(l+1)}{r^2} - 2\mathcal{V}\right] x = \int_0^r (\mathcal{W}^{(1)} - \mathcal{W}^{(2)})x\,ds \tag{14.32}$$

$$y'' + \left[k^2 - \frac{l(l+1)}{r^2} - 2\mathcal{V}\right] y = A(r) + \int_0^r (\mathcal{W}^{(1)} - \mathcal{W}^{(2)})y\,ds \tag{14.33}$$

The unknown constant $c$ can be found as before by substituting (14.31) into (14.29). The result is

$$c = \int_0^\infty Bx\,ds \Bigg/ \left(1 - \int_0^\infty By\,ds\right) \tag{14.34}$$

In variational calculations, exchange effects are taken into account by using a symmetrized trial function $\psi_t$ in the form

$$\psi_t = F_l(r_1)\psi_0(r_2) \pm F_l(r_2)\psi_0(r_1) \tag{14.35}$$

For example, we mention a variational calculation of the scattering length carried out in [37], where the trial function $f(r) = rF(r)$ was chosen in the form given by (13.24). The scattering lengths were found to be

$$a_+ = 8{\cdot}11, \qquad a_- = 2{\cdot}38 \tag{14.36}$$

## 15. THE EFFECT OF POLARIZATION OF THE ATOM ON THE SCATTERING OF AN ELECTRON

The effect of the polarization of an atom on the scattering of an electron may be investigated by including the term

$$\sum_\alpha \left(V_{0\alpha}F_\alpha + \int W_{0\alpha}F_\alpha\,dr\right)$$

in the equation for $F_0$ [see (10.55)]. In spite of the fact that this term is the sum over all the excited states $\alpha$, the polarization effect is not additive since in addition to the terms

$$V_{\alpha 0}F_0 + \int W_{\alpha 0}F_0\,dr$$

in the equation for $F_\alpha$ there are also the terms

$$\sum_{\alpha' \neq \alpha} \left(V_{\alpha\alpha'}F_{\alpha'} + \int W_{\alpha\alpha'}F_{\alpha'}\,dr\right)$$

which represent the coupling between the different states. The effect is additive only when this coupling is neglected and the coupling $0 \to \alpha$ is taken into account.

We shall show that in the limit of large $r$ the effect of excited states is equivalent to an additional interaction between the electron and the atom which can be characterized by a potential energy of the form $U = -\beta/r^4$ [27], where $\beta$ is the polarizability of the atom. We shall confine our attention to the approximation in which only the $0 \to \alpha$ coupling is taken into account. Under these conditions the system (10.55) becomes

$$\Delta F_0 + (k_0^2 - 2V_{00})F_0 - 2\int W_{00} F_0 \, dr' = 2 \sum_{\alpha \neq 0} \left( V_{0\alpha} F_\alpha + \int W_{0\alpha} F_\alpha \, dr' \right) \tag{15.1}$$

$$\Delta F_\alpha + (k_\alpha^2 - 2V_{\alpha\alpha})F_\alpha - 2\int W_{\alpha\alpha} F_\alpha \, dr' = 2\left( V_{\alpha 0} F_0 + \int W_{\alpha 0} F_0 \, dr' \right) \tag{15.2}$$

If the energy of the incident electron is such that excitation can take place, the right-hand side of (15.1) contains both the effect of polarization and the effect of coupling between excitation and scattering due to the unitary relation. But if the energy of the incident electron is insufficient for excitation, then the right-hand side of (15.1) contains only the polarization term. We shall begin with the latter case, i.e. we shall suppose that $k_\alpha^2 < 0$ for all $\alpha \neq 0$ and only $k_0^2 > 0$. Consider equation (15.2) for large $r$. If $k_\alpha < 0$, the solution of the homogeneous equation $\Delta F_\alpha + k_\alpha^2 F = 0$ which is finite for $r \to \infty$ will have the asymptotic form $\exp(-|k_\alpha| r)$. Under these conditions, the asymptotic behaviour of (15.2) is determined by the right-hand term. Since

$$k_\alpha^2 = k_0^2 + 2(E_0 - E_\alpha) \tag{15.3}$$

we have

$$\Delta F_\alpha + (k_0^2 - 2V_{\alpha\alpha})F_\alpha - 2\int W_{\alpha\alpha}(r', r) F_\alpha(r') \, dr' + 2(E_0 - E_\alpha) F_\alpha$$
$$= 2V_{\alpha 0} F_0 + 2\int W_{\alpha 0}(r', r) F_0(r') \, dr' \tag{15.4}$$

For large $r$ the expansion of $V_{\alpha 0}$ in terms of the reciprocal powers of $r$ begins with $r^{-l-1}$, where $l$ is the angular momentum characterizing the state $\alpha$ (when $l = 0$, $V_{\alpha 0}$ falls off exponentially with increasing $r$). The kernel of the exchange operator $W_{\alpha 0}$ falls off exponentially as $r \to \infty$. Therefore for large $r$ the right-hand side of equation (15.4) has the asymptotic form

$$r^{-l-1} \left( e^{ik_0 \nu . r} + q \frac{e^{ik_0 r}}{r} \right)$$

The leading term on the left-hand side of equation (15.4) for large $r$ is then $(E_0 - E_\alpha)F_\alpha$, so that we may assume that the asymptotic expression for $F_\alpha$ is

$$F_\alpha \sim -\frac{V_{\alpha 0} F_0}{E_\alpha - E_0} \tag{15.5}$$

It is easy to show that for this asymptotic behaviour of $F_\alpha$ the expression

$$(\Delta+k_0^2-2V_{\alpha\alpha})F_\alpha-2\int W_{\alpha\alpha}F_\alpha dr'$$

in equation (15.4) may be neglected when $r \to \infty$. In point of fact, according to equation (15.4), the term in $F_\alpha$ which exhibits the slowest variation is $r^{-l-1}\exp(ik_0\nu.r)$, whilst in

$$(\Delta+k_0^2-2V_{\alpha\alpha})F_\alpha-2\int W_{\alpha\alpha}F_\alpha dr'$$

the corresponding term is $r^{-l-2}\exp(ik_0\nu.r)$. We substitute (15.5) into (15.1) and let

$$U(r) = -\sum_{\alpha\neq 0}\frac{|V_{\alpha 0}(r)|^2}{E_\alpha-E_0} \tag{15.6}$$

$$W_p(r',r) = -\sum_{\alpha\neq 0}\frac{W_{0\alpha}(r',r)V_{\alpha 0}(r)}{E_\alpha-E_0} \tag{15.7}$$

We then have

$$\Delta F_0+(k_0^2-2V_{00}-2U)F_0 = 2\int (W_{00}+W_p)F_0\,dr' \tag{15.8}$$

In this equation $U$ enters as an addition to the potential energy due to excited states, while $W_p$ is an addition to the exchange operator. $V_{00}$, $W_{00}$ and $W_p$ fall off exponentially as $r \to \infty$. As regards $U$, we need only consider the slowly varying part, i.e. the dipole terms ($l = 1$). For large $r$, we then have

$$|V_{\alpha 0}|^2 \approx \frac{2}{3}\frac{1}{r^4}|r_{\alpha 0}|^2$$

(the factor 2/3 appears as a result of the integration with respect to angles within the matrix element), so that

$$U \sim -\frac{2}{3}\frac{1}{r^4}\sum_{\alpha\neq 0}\frac{|r_{\alpha 0}|^2}{E_\alpha-E_0} \tag{15.9}$$

The quantity $\beta=\frac{2}{3}\sum_{\alpha\neq 0}\frac{|r_{\alpha 0}|^2}{E_\alpha-E_0}$ is the polarizability of the hydrogen atom. Therefore, for large $r$, the function $U(r)$ tends to $-\beta/r^4$, which is the interaction energy between the electron and the induced dipole. Calculations [27] show that about 66% of $\beta$ is due to the $2p$-state. The discrete states contribute 81·4% in all, the remainder being due to the continuous spectrum. The numerical value of $\beta$ is 9/2.

Let us now return to the case where excitation is possible, i.e. one or more of the $k_\alpha^2$ are positive. We can substitute

$$F_\alpha = \tilde{F}_\alpha - \frac{V_{\alpha 0}F_0}{E_\alpha-E_0} \tag{15.10}$$

in equation (15.2) for the corresponding $\alpha$. The leading term in the asymptotic form of $\tilde{F}_\alpha$ will be the diverging wave $q_\alpha\frac{e^{ik_\alpha r}}{r}$. On substituting

(15.10) into (15.1), we have the following equation for $F_0(r)$

$$\begin{aligned}\Delta F_0+(k_0^2-2V_{00}-2U)F_0-2\int(W_{00}+W_p)F_0\,dr' \\ =2\sum_{\alpha\neq 0}\left(V_{0\alpha}\tilde{F}_a+\int W_{0\alpha}\tilde{F}_\alpha\,dr'\right)\end{aligned} \qquad (15.11)$$

When $r \to \infty$, the right-hand side of this equation expresses the coupling between elastic and inelastic scattering channels. Similarly to equation (15.8), the left-hand side includes the polarization interaction $U$.

The presence of the slowly decreasing potential ($\sim r^{-4}$) in (15.8) or (15.11) has an important effect on the asymptotic behaviour of the wave function. This can most easily be established in the limiting case of zero energy. For large $r$, the exchange terms fall off exponentially and are of little significance as far as the asymptotic expressions are concerned. We shall therefore consider the equation

$$\Delta F - V(r)F = 0$$

The function $F$ has the asymptotic form

$$F \sim 1 + \frac{\text{const}}{r}$$

For large $r$ we shall set

$$\Delta F = V(r)$$

and hence

$$F = 1 - \frac{1}{4\pi}\int \frac{V(r')\,dr'}{|r-r'|}$$

Completing the integration with respect to the angles we obtain

$$F = 1 - \frac{1}{r}\int_0^r Vr'^2\,dr' - \int_r^\infty Vr'\,dr'$$

or

$$F = 1 - \frac{1}{r}\int_0^\infty Vr'^2\,dr' - \int_r^\infty Vr'\,dr' + \frac{1}{r}\int_r^\infty Vr'^2\,dr'$$

which amounts to the same thing. The function

$$J = \int_r^\infty Vr'\,dr' - \frac{1}{r}\int_r^\infty Vr'^2\,dr' \qquad (15.12)$$

determines the nature of the approach to the asymptotic form.

If $V$ falls off as $\exp(-\lambda r)$ when $r \to \infty$, $J$ will also fall off exponentially:

$$J = e^{-\lambda r}\left(1 + \frac{1}{\lambda r}\right)$$

If, on the other hand, the polarization potential $V \sim r^{-4}$ is present, then

$$J = \frac{1}{2r^2}$$

In the absence of the polarization potential we have for large $r$

$$F \sim 1 + \frac{\text{const}}{r} + \text{const}\, e^{-\lambda r} \tag{15.13}$$

i.e. the approach to the asymptotic form is exponential. In the presence of the polarization potential,

$$F \sim 1 + \frac{\text{const}}{r} + \frac{\text{const}}{r^2} \tag{15.14}$$

and the asymptotic function is approached slowly in accordance with the $r^{-2}$ law.

It is possible to introduce polarization formally at finite distances, not only for $r \to \infty$. However, it will then no longer be a function of $r$ as given by equation (15.6) but an integral operator [42, 43]. We shall show this for the case of the simplified system of equations in which the exchange terms have been neglected. Thus we have

$$\Delta F_\alpha + (k_\alpha^2 - 2V_{\alpha\alpha})F_\alpha = 2V_{\alpha 0}F_0 \tag{15.15}$$

$$\Delta F_0 + (k_0^2 - 2V_{00})F_0 = 2\sum_\alpha V_{0\alpha}F_\alpha \tag{15.16}$$

We shall confine our attention to the case $k_\alpha^2 < 0$. Suppose that $G_\alpha$ is the resolvent defined by

$$\hat{G}_\alpha = (\Delta + k_\alpha^2 + i0 - 2V_{\alpha\alpha})^{-1} \tag{15.17}$$

The solution of (15.15) is then

$$F_\alpha = 2\hat{G}_\alpha V_{\alpha 0}F_0 \tag{15.18}$$

Substituting this into (15.16) and introducing the operator

$$\hat{U} = \sum_{\alpha \neq 0} V_{0\alpha}\hat{G}_\alpha V_{\alpha 0} \tag{15.19}$$

we have

$$\Delta F_0 + (k_0^2 - 2V_{00} - 2\hat{U})F_0 = 0 \tag{15.20}$$

Let us now consider the numerical calculations which include polarization effects. Calculations of the phase shifts for $L = 0, 1, 2$ with allowance for the $1s-2s$ coupling in the interval $0 \leqslant k^2 \leqslant 0{\cdot}75$ are given in [44] ($k^2 = 0{\cdot}75$ corresponds to the threshold for the excitation of the $2s$-level). Calculations in which the $1s-2s-2p$ coupling was taken into account are reported in [45]. When the $1s-2s$ coupling is allowed for, it is found that

$$a_+ = 7{\cdot}5, \qquad a_- = 2{\cdot}33$$

while the result for $1s-2s-2p$ coupling is

$$a_+ = 6{\cdot}74, \qquad a_- = 1{\cdot}89$$

The phase shifts $\delta_0^+$ and $\delta_0^-$ are plotted in Fig. 13. Calculations without polarization and with polarization allowed for by the variational method (see below) are given for comparison.

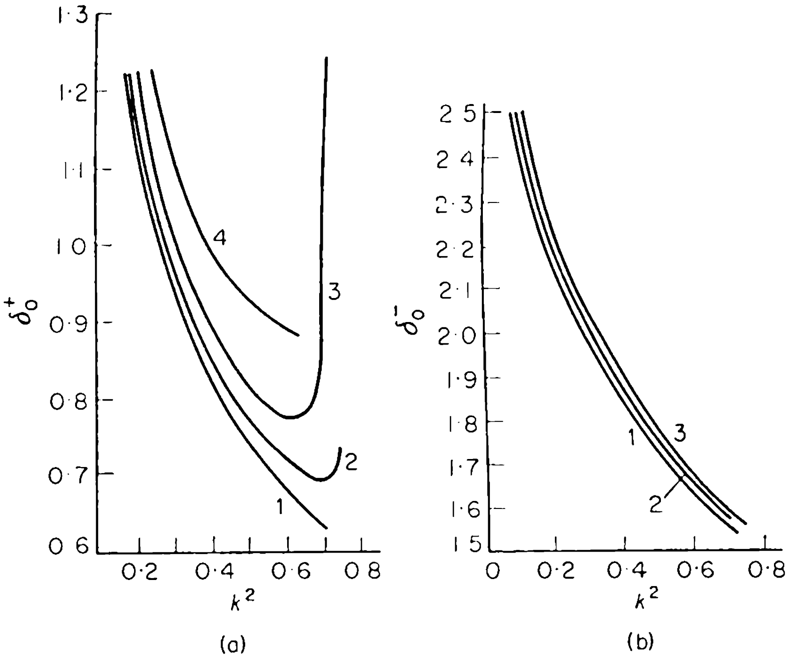


FIG. 13. The phase shifts $\delta_0^+$ (*a*) and $\delta_0^-$ (*b*): 1—without allowance for polarization, 2—with 1*s* — 2*s* coupling, 3—with 1*s* — 2*s* — 2*p* coupling, 4—variational method with polarization

The relative importance of the various couplings may be deduced from Table 3 which gives $\delta_0^+$ for two values of $k^2$. As can be seen, 1*s*—2*s* and 1*s*—2*p* coupling give rise to roughly the same contributions. The simultaneous inclusion of 2*s* and 2*p* states leads to a much greater contribution than the sum of the 1*s*—2*s* and 1*s*—2*p* contributions. Therefore, the 2*s*—2*p* coupling is significant and the effect of polarization is not additive.

TABLE 3

| States included | $\delta_0^+$ for $k^2$ equal to | |
|---|---|---|
| | 0·55 | 0·60 |
| 1*s* | 0·7004 | 0·6704 |
| 1*s* — 2*s* | 0·7352 | 0·7115 |
| 1*s* — 2*p* | 0·7338 | 0·7040 |
| 1*s* — 2*s* — 2*p* | 0·7846 | 0·7707 |
| 1*s* — 2*s* — 2*p* — 3*s* | 0·7894 | 0·7738 |
| 1*s* — 2*s* — 2*p* — 3*p* | 0·7920 | 0·7738 |
| 1*s* — 2*s* — 2*p* — 3*d* | 0·7841 | 0·7694 |
| 1*s* — 2*s* — 2*p* —3*s* — 3*p* | 0·7975 | 0·7814 |

Another feature evident from Table 3 is that the coupling with the 3*s*, 3*p* and 3*d* states adds very little to the contribution due to the 1*s*−2*s*−2*p* coupling. On the other hand, it cannot be considered that the inclusion of only the 2*s* and 2*p* states is sufficient since the contribution to static polarizability of the hydrogen atom due to the 2*p* state is 66%. It should therefore be assumed that the convergence is very slow and a large number of excited states must be taken into account to improve the approximation which is achieved with the 1*s*−2*s*−2*p* coupling only.

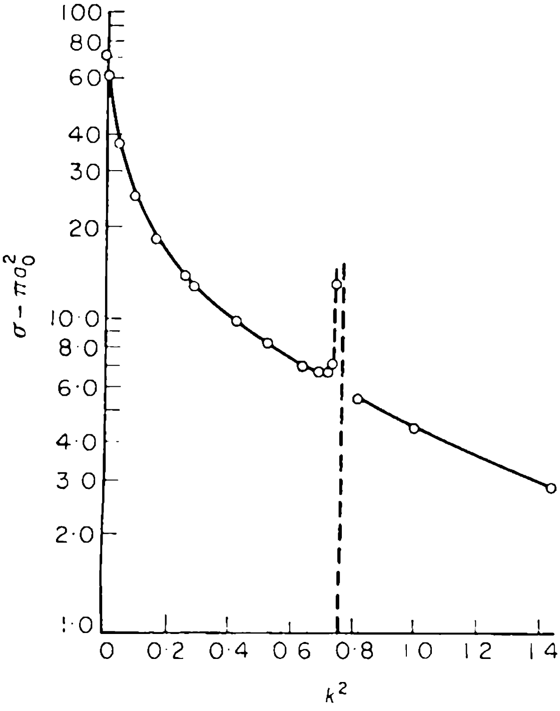


FIG. 14. Peak in the elastic scattering cross-section [44]

As can be seen from Fig. 13, the phase shift increases very rapidly near the threshold for the excitation of the 2*s*-level. The variation in the phase shift in the region of rapid increase can be described by the Breit-Wigner formula with resonance energy $E = 9{\cdot}61$ eV ($k^2 = 0{\cdot}711$) and a full width at half height $\Gamma = 0{\cdot}109$ eV [45]. As can be seen, this is a very narrow resonance whose presence is predicted by the general theory (§ 12). In addition, there is also a threshold peak. Figure 14 shows the scattering cross-section as a function of energy with a clearly defined peak [44]. Analogous results, i.e. the narrow resonance, were reported in [34]. It should be noted that detailed analysis of the variation in the phase near the 2*s* excitation threshold was made difficult in [44, 45] because the convergence of the iteration method used to solve the integro-differential equations deteriorated as threshold was approached. It is evident from Fig. 13 that the phase shift $\delta_0^-$ is not modified to any great extent when the $1s-2s-2p$ coupling is taken into account. Figure 15 shows $k$ cot $\delta_0^\pm$ as a function of $k^2$. As can be seen, $k$ cot $\delta_0^-$ is appreciably non-linear for small $k^2$. This is due to the terms $k$ and $k^2 \ln k$ in equation (3.24). In the case of $k$ cot $\delta_0^+$ the departure from linearity is very slight.

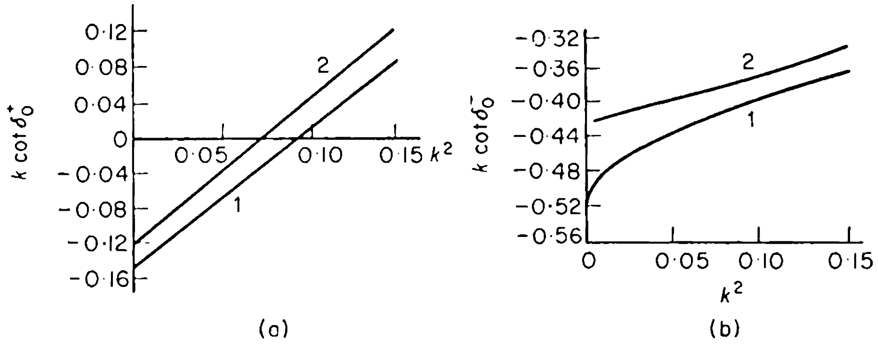


FIG. 15. Dependence of $k \cot \delta_0{}^+$ (*a*) and $k \cot \delta_0{}^-$ (*b*) on $k^2$: 1—with $1s-2s-2p$ coupling, 2—without polarization

This is due to the fact that the coefficient of $k$ is inversely proportional to the square of the scattering length and is therefore much smaller in the singlet state than in the triplet state.

Figure 16 shows the phase shifts $\delta_1^\pm$ and $\delta_2^\pm$.† Here again one can see a rapid increase in the phase near the threshold for the excitation of the

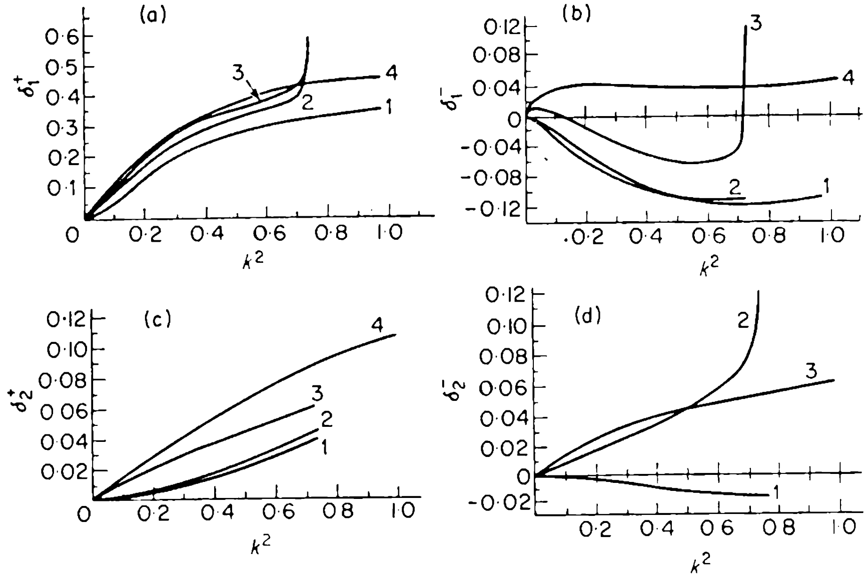


FIG. 16. The phase shifts $\delta_1{}^+$ (*a*), $\delta_1{}^-$ (*b*), $\delta_2{}^+$ (*c*) and $\delta_2{}^-$ (*d*): 1—without polarization, 2—with $1s-2s$ coupling, 3—with $1s-2s-2p$ coupling, 4—by the method of polarized orbitals

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† For comparison, the results of calculations including the polarization effects and using a different method are also given (see below).

2s-level. As has been pointed out in [45], the phase shifts $\delta_2^+$ and $\delta_2^-$ approach each other at low energies and are adequately represented by equation (3.25) if $\beta$ is replaced by 66% of the true polarizability of the hydrogen atom, i.e. by the contribution due to the 2p state. Thus, when $k^2 = 0{\cdot}1$ the values of $\delta_2^\pm$ calculated in [45] are $\delta_2^+ = 0{\cdot}0084$ and $\delta_2^- = 0{\cdot}0096$, whereas equation (3.25) yields $\delta_2 = 0{\cdot}0089$.

There is another way of including the polarization effects. In this method the basic functions for the expansion of the wave function of the atom + electron system are taken to be the wave functions of the atomic electron in the field of two centres of force, i.e. the nucleus and the incident electron, rather than the atomic wave function as in (10.17) or (10.46) [46]. This method is a development of the so-called method of perturbed stationary states described in the book of Mott and Massey. In [46] it is referred to as the method of polarized orbitals.

We first consider the elastic scattering in the absence of exchange. We shall write the wave function for the atom + electron system in the form

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = F(\boldsymbol{r}_1)\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{15.21}$$

where $F(\boldsymbol{r}_1)$ describes the incident electron and $\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ describes the atomic electron in the field of the nucleus and the incident electron. The function $\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ can in its turn be written as the sum

$$\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_0(\boldsymbol{r}_2) + g(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{15.22}$$

where $\psi_0(\boldsymbol{r}_2)$ is the wave function of the atomic electron in the isolated atom and $g(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the change in the atomic function at $\boldsymbol{r}_2$ due to the incident electron at $\boldsymbol{r}_1$. The equation for $F$ can be obtained from equation (10.24):

$$\int \psi_0(\boldsymbol{r}_2)(H-\mathscr{E})\psi(\boldsymbol{r}_1, \boldsymbol{r}_2)\, d\boldsymbol{r}_2 = 0 \tag{15.23}$$

where $\mathscr{E} = \frac{1}{2}k^2 + E_0$ and the energy of the ground state of the atom is $E_0 = -\frac{1}{2}$.

We substitute the expression for $H$ given by (9.1) and the expression for $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ given by (15.22) into (15.23). We shall, moreover, require that $g(\boldsymbol{r}_1, \boldsymbol{r}_2)$ and $\psi_0(\boldsymbol{r}_2)$ should be orthogonal for all $\boldsymbol{r}_1$:

$$\int g(\boldsymbol{r}_1, \boldsymbol{r}_2)\psi_0(\boldsymbol{r}_2)\, d\boldsymbol{r}_2 = 0$$

We then have

$$\Delta F + (k^2 - 2V - 2V_p)F = 0 \tag{15.24}$$

where $V$ is the potential energy of the electron in the field of the undisturbed atom given by (13.2) and $V_p$ is the polarization correction to the potential energy and is given by

$$V_p(\boldsymbol{r}_1) = \int \frac{\psi_0(\boldsymbol{r}_2)g(\boldsymbol{r}_1, \boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}\, d\boldsymbol{r}_2 \tag{15.25}$$

The problem is therefore reduced to the determination of the function $g(\boldsymbol{r}_1, \boldsymbol{r}_2)$.

The equation for $g(r_1, r_2)$ can be obtained by substituting (15.21) and (15.22) into $(H-\mathscr{E})\psi(r_1, r_2) = 0$ and using (15.24) and the equation satisfied by $\psi_0(r_2)$. In the present method, the determination of $g(r_1, r_2)$ is carried out on the adiabatic approximation in which the position of the incident electron $r_1$ is regarded as fixed and all the derivatives of $g(r_1, r_2)$ with respect to $r_1$ are equated to zero. Moreover, if it is assumed that $g$ is a small correction to $\psi_0$, the determination of $g(r_1, r_2)$ can be simplified still further and $g$ can be neglected in all the terms into which the sum $\psi_0+g$ enters. We then have the equation for $g$

$$\left(\tfrac{1}{2}\Delta_2 + \frac{1}{r_2} - \tfrac{1}{2}\right) g(r_1, r_2) = \left[\frac{1}{|r_1 - r_2|} - \frac{1}{r_1} - V(r_1)\right] \psi_0(r_2) \qquad (15.26)$$

An accurate solution of this equation can only be found by numerical integration. However, the asymptotic behaviour of $g$ for $r_1 \gg r_2$ can be found in analytical form. When $r_1 \to \infty$ the potential $V(r_1)$ falls off exponentially and we can neglect $V(r_1)$ on the right-hand side of (15.26). Next, if we expand $|r_1 - r_2|^{-1}$ in terms of the spherical harmonics and retain the dipole term only, we have

$$\frac{1}{|r_1 - r_2|} - \frac{1}{r_1} \approx \frac{r_2}{r_1^2} \cos\theta \qquad (15.27)$$

where $\theta$ is the angle between $r_1$ and $r_2$. When these simplifications are introduced, equation (15.26) is replaced by the asymptotic equation

$$\left(\tfrac{1}{2}\Delta_2 + \frac{1}{r_2} - \tfrac{1}{2}\right) g_0(r_1, r_2) = 2\frac{r_2}{r_1^2} \psi_0(r_2) \cos\theta \qquad (15.28)$$

where $g_0$ is the asymptotic function. The solution of this equation is

$$g_0(r_1, r_2) = \frac{\cos\theta}{r_1^2\sqrt{\pi}} e^{-r_2}(r_2 + \tfrac{1}{2}r_2^2) \qquad (15.29)$$

This solution can be augmented by the solution of the homogeneous equation obtained from (15.28) by rejecting the right-hand side. However, since $g$ and $\psi_0$ are orthogonal, the additional function is equal to zero.

As regards the approximate solution of (15.26), we must first mention [47] which gives a variational method of solving this equation. The method is based on the fact that the function

$$I = \int g(r_1, r_2) \left[\left(\Delta_2 + \frac{2}{r_2} - 1\right) g(r_1, r_2) - \frac{2}{|r_1 - r_2|} \psi_0(r_2)\right] dr_2 \qquad (15.30)$$

is a minimum with respect to an arbitrary variation of $g$ (for any $r_1$), and its stationary value is equal to the polarization potential $V_p$ given by equation (15.25). Another approximation is described in [46], where the polarization potential is calculated by replacing $g$ by its asymptotic form $g_0$ for $r_1 \geqslant r_2$

and assuming $g = 0$ for $r_1 < r_2$:

$$g = \varepsilon(r_1, r_2) g_0$$

$$\varepsilon = \begin{cases} 1 & r_1 \geqslant r_2 \\ 0 & r_1 < r_2 \end{cases} \tag{15.31}$$

Having determined $g(r_1, r_2)$ by any of these approximate methods we can calculate the polarization correction to the electron–atom interaction energy from equation (15.25).

In order to take the exchange effect into account we must construct the symmetrized function

$$\psi(r_1, r_2) = F(r_1)[\psi_0(r_2) + g(r_1, r_2)] \pm F(r_2)[\psi_0(r_1) + g(r_2, r_1)] \tag{15.32}$$

where $g$ satisfies (15.26) as before. Substituting equation (15.32) into (15.23), we obtain an equation of the form

$$\Delta F + (k^2 - 2V - 2V_p)F = 2\int (W + W_p) F \, dr' \tag{15.33}$$

where $W_p$ is the polarization correction to the exchange operator. As before, the angular variables of this equation can now be separated and equations with radial functions obtained.

The equations derived from the approximate expression (15.31) for $g$ are [46]:

$$\frac{d^2 f_l}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2} - 2\mathcal{V}\right] f_l - \int_0^\infty \mathcal{W}_{ll}(r', r) f_l \, dr'$$
$$= 2\frac{9}{2}\frac{1}{r^4} f_l + N(r) f_l \mp P(f_l) \tag{15.34}$$

where $\mathcal{V}$ and $\mathcal{W}_{ll}$ are given by equations (13.2) and (14.4).

The right-hand side contains terms describing the polarization effect. The first term contains $9/2r^4$, i.e. it is the asymptotic form of the polarization potential with which we are already familiar. The remaining terms are:

$$N = -\tfrac{3}{2} e^{-2r}\left(r^5 + \tfrac{9}{2}r^4 + 9r^3 + \tfrac{27}{2}r^2 + \tfrac{27}{2}r + \tfrac{27}{4}\right) \tag{15.35}$$

$$\begin{aligned} P(f_l) = {} & \tfrac{2}{3}(1 + k^2)\delta_{l1} \int_r^\infty \frac{e^{-r} f_l(r)\, dr}{r^2} \\ & + 4\left[\frac{l}{(2l+1)(2l-1)} r^{-l-1} \int_r^\infty \frac{e^{-r} f_l(r)\, dr}{r^{l+2}}\right. \\ & \left. + \frac{(l+1) r^{l+1}}{(2l+1)(2l+3)} \int_r^\infty \frac{e^{-r} f_l(r)\, dr}{r^{l+4}}\right] e^{-r}\left(r + \tfrac{1}{2}r^2\right) \\ & + \tfrac{4}{3} r^2 e^{-r} \delta_{l1} \int_r^\infty \frac{e^{-r} f_l(r)}{r^2}\, dr \end{aligned} \tag{15.36}$$

The equations (15.34) are transformed to a form not requiring iteration and solved numerically for $l = 0, 1, 2$ and $k$ between 0 and 1. The wave functions are calculated up to $r = 20$ after which they are assumed to be identical with the asymptotic form

$$\sin\left(kr - \frac{l\pi}{2} + \delta_l\right)$$

Figure 16 shows plots of $\delta_1^{\pm}$ and $\delta_2^{\pm}$. The scattering lengths are found to be $a^+ = 5{\cdot}8$, $a^- = 1{\cdot}9$, whereas the corresponding values without the polarization corrections are respectively 8·1 and 2·35. However, subsequent calculations [48] show that even for $r > 20$ there is an appreciable contribution due to the polarization potential. The change in the phase shift $\delta_0$ between $r = 20$ and $r = \infty$ can most easily be determined from equation (3.35) which for $l = 0$ is of the form

$$\frac{d\delta_0}{dr} = -\frac{2V}{k}\sin^2(kr+\delta_0) \tag{15.37}$$

For $r > 20$ all the exchange terms in (15.34) are practically zero and this equation is valid. At such large distances we need only retain the asymptotic part $\beta/r^4$ in the potential $V$. If, in $\sin^2(kr+\delta_0)$, we replace $\delta_0(r)$ by its limiting value $\delta_0(\infty)$ which is valid for small changes in the phase shift, we have

$$\delta_0(\infty)-\delta_0(R) = \frac{2\beta}{k}\int\limits_R^{\infty}\frac{\sin^2[kr+\delta_0(\infty)]}{r^4}\,dr \tag{15.38}$$

Hence, to within terms of the order of $k$,

$$\frac{1}{k}[\delta_0(\infty)-\delta_0(R)] = \left(\frac{\beta}{3}\frac{a^2}{R^3} - \beta\frac{a^2}{R^2} + \beta\frac{1}{R}\right) + k\frac{\pi\beta}{3} + o(k^2\ln k) \tag{15.39}$$

where $a$ is the exact scattering length. This formula was derived in another way in [48].

We note that equation (15.39) contains the linear term $k\pi\beta/3$ which is identical with the linear term in equation (3.24). When $k = 0$ we obtain the relation between the accurate scattering length $a$ and the scattering length $a(R)$ which is obtained from the asymptotic form for $R = 20$:

$$a = a(R)-\beta\left(\frac{1}{3}\frac{a^2}{R^3} - \frac{a}{R^2} + \frac{1}{R}\right) \tag{15.40}$$

Calculations yield $a^- = 1{\cdot}74$. The correction to the singlet scattering length $a^+$ is less significant because $a^+$ is small.

In variational calculations, polarization is taken into account by including in the trial function terms containing $r_{12} \equiv |r_1 - r_2|$, so that $\psi(r_1, r_2)$ is not reduced to the symmetrized combination of the products of functions of $r_1$ and functions of $r_2$ of the form given by equation (14.35).

Determination of the scattering length is particularly important in variational calculations. In the case of scattering of an electron by an atom, it turns out, just as in the simpler case of scattering by a central force (§ 7), that the scattering length calculated by Kohn's method is the upper bound on the true scattering length [49]. This provides us with a criterion for estimating the accuracy of the variational calculations. In the triplet state we have $a^- \leqslant a_K^-$ where $a_K^-$ is Kohn's scattering length:

$$a_K^- = a_t^- + 2\int \psi_t(H-E_0)\psi_t \, d\tau \tag{15.41}$$

$H$ is the energy operator for the electron + atom system, $E_0$ is the ground state energy of the hydrogen atom, $\psi_t$ is the trial function whose asymptotic form is

$$\psi_t^- = (1-P_{12})\psi_0(r_2)\left(\frac{a_t}{r_1} - 1\right) \tag{15.42}$$

and $\psi_0$ is the atomic wave function.

In the singlet state, we have the following inequality which is analogous to (7.29):

$$a^+ \leqslant a_t^+ + 2\int \psi_t^+(H-E_0)\psi_t^+ \, d\tau - \frac{2}{E'-E_0}\left|\int \psi'(H-E_0)\psi_t^+ \, d\tau\right|^2 \tag{15.43}$$

where $\psi'$ and $E'$ are the eigenfunction and energy eigenvalue of the bound state of the electron + atom system (it is assumed that there is only one such state). The function $\psi'$ must be a sufficiently good approximation to the eigenfunction for the negative hydrogen ion in order to ensure that

$$E' \equiv \int \psi' H \psi' \, d\tau < E_0 \tag{15.44}$$

The inequality given by (15.43) can also be written in the form

$$a^+ \leqslant a_k^+ \tag{15.45}$$

provided that one uses the function $\psi$ varied by Kohn's method and including the bound-state function $\psi'$, so that

$$\psi_t = \tilde{\psi}_t + A\psi' \tag{15.46}$$

where $A$ is the varied parameter.

It is shown in [49] that even if the function $\psi$ does not have the structure indicated by equation (15.46), the inequality given by (15.45) is still obeyed under certain conditions.

We now briefly review the numerical calculations. The most systematic are given in [50]. The $s$-wave phase shift was calculated from the wave function $\psi$ for the electron + atom system of the form

$$\psi = \varphi + \chi$$

where

$$\varphi = \frac{1}{\sqrt{2}}(1 \pm P_{12})2e^{-r_2}\frac{1}{4\pi r_1}f(r_1) \tag{15.47}$$

and

$$f(r_1) = \frac{1}{k_1}\sin kr_1 + \lambda\frac{\cos kr_1}{k}\left(1-e^{-\frac{\kappa}{2}r_1}\right) \tag{15.48}$$

$$\chi = \sum_{l,m,n>0} C_{l,m,n}\, e^{-\kappa\frac{r_1+r_2}{2}}\, r_{12}^{l}(r_1^m r_2^n \pm r_1^n r_2^m) \tag{15.49}$$

The function $\frac{1}{k}\tan\delta$ was defined as the stationary value of the functional

$$\frac{1}{k}\mathrm{tg}\,\delta = \lambda - \int \psi(H-E)\psi\, dr_1\, dr_2 \tag{15.50}$$

The set of numbers $l, m, n$ in equation (15.49) was chosen so that the sum $l+m+n$ varied between 2 and 7 in the triplet state and between 1 and 6 in the singlet state. Correspondingly, the coefficients $C_{l,m,n}$ formed matrices of rank 3, 7, 13, 22, 34 and 50.

Figure 17 shows the stationary state values of $-\frac{1}{k}\tan\delta_0$ for the triplet $s$-wave with $k = 0{\cdot}4$ (about 2 eV) as a function of the scale parameter $\kappa$.

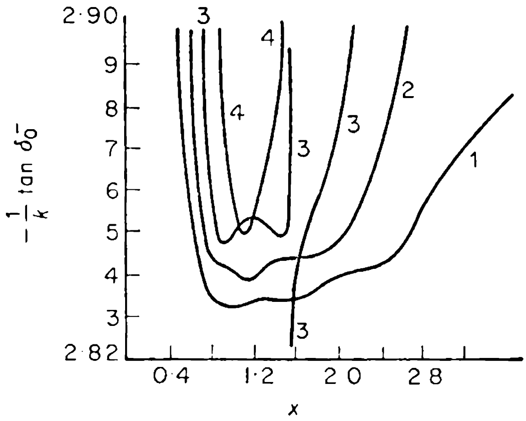


FIG. 17. Dependence of $-(1/k)\tan\delta_0^-$ on the scale parameter $\kappa$ for $k = 0{\cdot}4$; the numbers indicated on the curves correspond to matrices of the following rank: 34 (1), 15 (2), 7 (3) and 3 (4)

When $\kappa = 1{\cdot}55$, the curve corresponding to the matrix of rank 7 exhibits a discontinuity. Similar properties are exhibited by all matrices of higher rank but they are so narrow that they have not been resolved.

When the number of parameters is large, the curves become smoother and approach each other. If it is assumed that as the number of parameters is increased all the curves tend to a single common curve, then it is possible to determine the corresponding phase shifts by extrapolation. Figure 12 shows the extrapolated phase shifts for the triplet and singlet states.

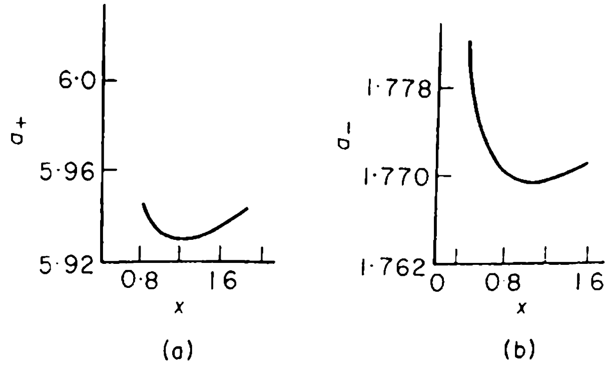
For the calculation of the scattering length the function $\varphi$ was chosen in the form

$$\varphi = (1 \pm p_{12}) 2e^{-r_2} \left[ 1 - \frac{a}{r_1} f_1 - \frac{2{\cdot}25}{r_1^2} f_2 - \frac{r_1^2 + r_2^2}{2r_1^2} f_3 \cos\theta \right] \qquad (15.51)$$

where

$$f_n = r_1^n \int_0^1 \frac{p^{n-1}\,dp}{(n-1)!} e^{-pr_1} \qquad (n = 1, 2, 3)$$

The dependence of $\varphi$ on $r_1$ was chosen so as to reflect correctly the effect of the polarization of the atom on the asymptotic form of the wave function. Figure 18 shows the scattering length as a function of the parameter $\kappa$.



(a) (b)

FIG. 18. Scattering lengths $a_+$ and $a_-$ as functions of the parameter $\kappa$.

Table 4 gives a summary of the scattering lengths calculated by the various methods.

TABLE 4

| | $1s - 2s - 2p$ coupling | Method of polarized orbitals | Variational method |
|---|---|---|---|
| $a_+$ | 6·74 | 5·8 | 5·961 |
| $a_-$ | 1·89 | 1·74 | 1·768 |

## 16. DISPERSION RELATIONS FOR THE SCATTERING AMPLITUDE IN THE CASE OF THE HYDROGEN ATOM

The dispersion relations for the scattering amplitude in the case of the scattering of an electron by the hydrogen atom can be deduced by means of an analysis analogous to § 4 [51, 52]. As in § 4 the dispersion relations are based on the properties of the Green's function $G(E+E_0+i0)$ for the atom + electron system, where $E$ is the energy of the incident electron, and $E_0$ is the energy of the hydrogen atom in the ground state. We shall assume, by analogy with the scattering of a particle by a centre of force, that $G(E+E_0+i0)$ is an analytic function in the plane of the complex variable $E$ with a cut along the positive real axis, and has simple poles on the negative real axis at the points $E=-|E_j|$ which correspond to the bound states of the negative hydrogen ion $H^-$. The residues at these points are equal to $u_j(\mathbf{r}_1,\mathbf{r}_2)u_j^*(\mathbf{r}'_1,\mathbf{r}'_2)$ where $u_j(\mathbf{r}_1,\mathbf{r}_2)$ is the eigenfunction of $H^-$. Moreover, there are branch points on the real positive axis which correspond to thresholds for the excitation of the atomic levels.

Using the expressions given by (10.14) and (10.16) for the direct and exchange amplitudes, and substituting the expression for $\psi$ through the resolvent $\hat{G}$ into these expressions, we have from (10.1)

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=e^{ik\mathbf{v}.\mathbf{r}_2}\psi_0(\mathbf{r}_1)-\hat{G}(E+E_0+i0)[V_0(\mathbf{r}_2)+V(\mathbf{r}_1,\mathbf{r}_2)]\,e^{ik\mathbf{v}.\mathbf{r}_2}\psi_0(\mathbf{r}_1) \tag{16.1}$$

Since we are interested in the forward scattering amplitude, we shall set $\mathbf{v}=\mathbf{n}$. This yields

$$f=f_0+\frac{1}{2\pi}\int e^{-ik\mathbf{v}.\mathbf{r}'_2}\psi_0^*(\mathbf{r}'_1)[V_0(\mathbf{r}'_2)+V(\mathbf{r}'_1,\mathbf{r}'_2)]$$
$$\times\hat{G}(E+E_0+i0)[V_0(\mathbf{r}'_2)+V(\mathbf{r}'_1,\mathbf{r}'_2)]\,e^{ik\mathbf{v}.\mathbf{r}'_2}\psi_0(\mathbf{r}'_1)\,d\mathbf{r}'_1\,d\mathbf{r}'_2 \tag{16.2}$$

and

$$g=g_0+\frac{1}{2\pi}\int e^{-ik\mathbf{v}.\mathbf{r}'_1}\psi_0^*(\mathbf{r}'_2)[V_0(\mathbf{r}'_1)+V(\mathbf{r}'_1,\mathbf{r}'_2)]$$
$$\times\hat{G}(E+E_0+i0)[V_0(\mathbf{r}'_2)+V(\mathbf{r}'_1,\mathbf{r}'_2)]\,e^{ik\mathbf{v}.\mathbf{r}'_2}\psi_0(\mathbf{r}'_1)\,d\mathbf{r}'_1\,d\mathbf{r}'_2 \tag{16.3}$$

where

$$f_0=-\frac{1}{2\pi}\int[V_0(\mathbf{r}'_2)+V(\mathbf{r}'_1,\mathbf{r}'_2)]|\psi_0(\mathbf{r}'_1)|^2\,d\mathbf{r}'_1\,d\mathbf{r}'_2 \tag{16.4}$$

$$g_0=-\frac{1}{2\pi}\int[V_0(\mathbf{r}'_1)+V(\mathbf{r}'_1,\mathbf{r}'_2)]\,e^{ik\mathbf{v}.(\mathbf{r}_2'-\mathbf{r}_1')}\psi_0(\mathbf{r}'_1)\psi_0^*(\mathbf{r}'_2)\,d\mathbf{r}'_1\,d\mathbf{r}'_2 \tag{16.5}$$

The functions $f_0$ and $g_0$ are real and can readily be given in an explicit form.

For $f-f_0$ and $g-g_0$ we have expressions analogous to (4.16):

$$\mathrm{Re}f=f_0+\frac{1}{\pi}\mathscr{P}\int_0^\infty dE'\frac{\mathrm{Im}f(E')}{E-E'}-\sum_j\frac{d_j}{E+|E_j|} \tag{16.6}$$

and

$$\mathrm{Re}\,g=g_0+\frac{1}{\pi}\mathscr{P}\int_0^\infty dE'\frac{\mathrm{Im}\,g(E')}{E-E'}-\sum_j\frac{c_j}{E+|E_j|} \tag{16.7}$$

where

$$d_j = \frac{1}{2\pi}\int e^{-\kappa_j \mathbf{v}.\mathbf{r}_1}\psi_0(\mathbf{r}_2)[V_0(\mathbf{r}_1)+V(\mathbf{r}_1,\mathbf{r}_2)]u_j(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2$$

$$\times\int e^{-\kappa_j \mathbf{v}.\mathbf{r}'_1}\psi_0(\mathbf{r}'_2)[V_0(\mathbf{r}'_1)+V(\mathbf{r}'_1,\mathbf{r}'_2)]u_j^*(\mathbf{r}'_1,\mathbf{r}'_2)d\mathbf{r}'_1\,d\mathbf{r}'_2 \qquad (16.8)$$

$$c_j = \frac{1}{2\pi}\int d\mathbf{r}_1\,d\mathbf{r}_2\,e^{-\kappa_j \mathbf{v}.\mathbf{r}_2}\psi_0(\mathbf{r}_1)[V_0(\mathbf{r}_2)+V(\mathbf{r}_1,\mathbf{r}_2)]u_j(\mathbf{r}_1,\mathbf{r}_2)$$

$$\times\int d\mathbf{r}'_1\,d\mathbf{r}'_2\,e^{-\kappa_j \mathbf{v}.\mathbf{r}'_1}\psi_0(\mathbf{r}'_2)[V_0(\mathbf{r}'_1)+V(\mathbf{r}'_1,\mathbf{r}'_2)]u_j(\mathbf{r}'_1,\mathbf{r}'_2) \qquad (16.9)$$

and $\mathscr{P}$ represents the principal value of the integral, while $\kappa_j = \sqrt{2|E_j|}$.

The singlet ground state of the negative hydrogen atom (binding energy ~0·7 eV) is well known at the present time. There are grounds for supposing that $H^-$ does not have excited states. We shall continue our analysis on the assumption that there is only one singlet state. In this state the function $u_j(\mathbf{r}_1, \mathbf{r}_2)$ is symmetric and therefore we have from (16.9) and (16.8)

$$c = d = \frac{1}{2\pi}\left|\int e^{-\kappa \mathbf{v}.\mathbf{r}_1}\psi_0(\mathbf{r}_2)[V_0(\mathbf{r}_1)+V(\mathbf{r}_1,\mathbf{r}_2)]u(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2\right|^2 \qquad (16.10)$$

Substituting the symmetric and antisymmetric combinations of $f$ and $g$ and using (10.45) we have

$$\operatorname{Re} q^+ = q_0^+ + \frac{1}{4\pi^2}\mathscr{P}\int \frac{k'\sigma^+(E')}{E'-E}\,dE' - \frac{2c}{E+|E_1|} \qquad (16.11)$$

$$\operatorname{Re} q^- = q_0^- + \frac{1}{4\pi^2}\mathscr{P}\int_0^\infty dE'\,\frac{k'\sigma^-(E')}{E'-E} \qquad (16.12)$$

As was to be expected, the singlet bound state of the negative hydrogen ion has an effect on the singlet scattering amplitude $q^+$ but has no effect on the triplet amplitude $q^-$. For comparison with experiment one must use a formula for the cross-section $\langle\sigma\rangle$ which is equal to $\frac{3}{4}\sigma^- + \frac{1}{4}\sigma^+$. It is readily shown that

$$\frac{k}{4\pi}\langle\sigma\rangle = \operatorname{Im}(f - \tfrac{1}{2}g) \qquad (16.13)$$

The dispersion relation for $f - \frac{1}{2}g$ is

$$\operatorname{Re}(f-\tfrac{1}{2}g) = (f-\tfrac{1}{2}g)_0 + \frac{1}{4\pi^2}\int_\infty^\infty dE'\,\frac{k'\langle\sigma(E')\rangle}{E'-E} - \frac{c}{2(E+|E_1|)} \qquad (16.14)$$

At zero energy (16.14) yields the following expression for the scattering lengths:

$$\tfrac{3}{4}a^- + \tfrac{1}{4}a^+ = (f-\tfrac{1}{2}g)_0 - \frac{1}{2\pi^2}\int_0^\infty \langle\sigma\rangle\,dk + \frac{c}{2|E|} \qquad (16.15)$$

An interesting example of the application of (16.15) is the analysis of the two contradictory experiments on the scattering of electrons by hydrogen atoms [53, 54] which is given in [52]. The analysis is based on the comparison of the values of $\int_0^\infty \langle\sigma\rangle\, dk$ from (16.15) and the same quantity determined from experimental data.

First we note that because $a^+$ and $a^-$ are positive we have immediately the inequality

$$\int_0^\infty \langle\sigma\rangle\, dk \leqslant 2\pi^2\left(\frac{c}{2|E_1|}+f_0-\tfrac{1}{2}g_0\right) \tag{16.16}$$

If we now calculate $f_0$ and $g_0$ from (16.4) and (16.5) we have

$$f_0-\tfrac{1}{2}g_0=-2 \tag{16.17}$$

The quantity $c/2|E_1|$ cannot be calculated exactly since the wave function for the ground state of the $H^-$ ion is not known. It is pointed out in [51] that the approximate values available for this quantity vary by about 20%, depending upon which approximation is used for the wave function of $H^-$. Using calculated values for the quantities on the right-hand side of (16.16) we have

$$\int_0^\infty \langle\sigma\rangle\, dk < 7{\cdot}52 \tag{16.18}$$

On substituting the values of $a^+$ and $a^-$ calculated in [46, 48] into (16.15) we obtain

$$\int_0^\infty \langle\sigma\rangle\, dk = 4{\cdot}77 \tag{16.19}$$

Let us now return to the determination of $\int_0^\infty \langle\sigma\rangle\, dk$ with the aid of experimental data. This was done in [51] by the following procedure. At low energies ($\lesssim$ 10 eV) use was made of the experimental data on elastic scattering of electrons by hydrogen atoms. At high energies ($\gtrsim$ 500 eV) the determination was based on the values calculated on the Born approximation. The cross-section $\langle\sigma\rangle$ in the intermediate region was determined by interpolation. The uncertainty in $\int_0^\infty \langle\sigma\rangle\, dk$ due to interpolation errors can be estimated quite easily, and the final result is

$$\frac{1}{2\pi^2}\int_0^\infty \langle\sigma\rangle\, dk = 10{\cdot}3 \pm 0{\cdot}5 \tag{16.20}$$

when we use the results of [53], and

$$\frac{1}{2\pi^2}\int_0^\infty \langle\sigma\rangle\, dk = 5{\cdot}1 \pm 0{\cdot}5 \qquad (16.21)$$

when we use the results of [54].

As can be seen, (16.20) lies well above (16.18), whereas (16.21) is in agreement with (16.18) and (16.19).

## 17. ANGULAR DISTRIBUTION OF ELECTRONS AND THE SCATTERING CROSS-SECTION. COMPARISON WITH EXPERIMENT

In this section we shall consider the differential scattering cross-sections averaged over the spins and calculated from the phase shifts $\delta_0^\pm$, $\delta_1^\pm$ and $\delta_2^\pm$ with allowance for the $1s-2s-2p$ coupling for four values of the energy [45]. The corresponding curves are shown in Fig. 19. The points in this figure represent the experimental data on the angular distribution as reported in [54, 55].

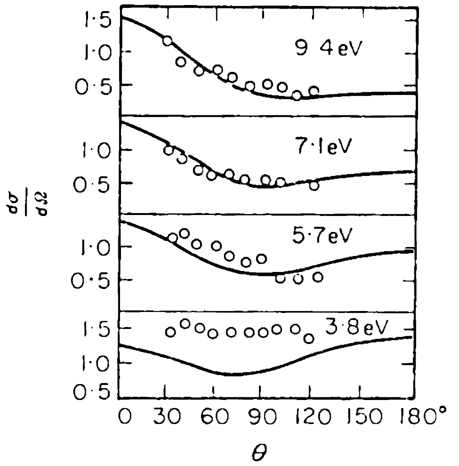


FIG. 19. The differential scattering cross-section

$$\frac{d\sigma}{d\Omega} = \frac{1}{4}\frac{d\sigma^+}{d\Omega} + \frac{3}{4}\frac{d\sigma^-}{d\Omega}$$

in units of $\pi a_0^2$

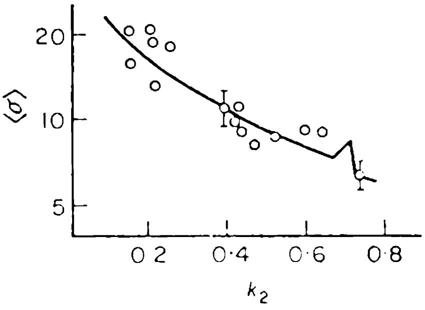


FIG. 20. The elastic scattering cross-section

$$\langle\sigma\rangle = \tfrac{3}{4}\sigma_- + \tfrac{1}{4}\sigma_+$$

in units of $\pi a_0^2$

One notes the characteristic form of the angular distribution of the scattered electrons. At low energies ($\approx$ 3 eV) forward and backward scattering predominate. This effect is due to the exchange interaction. As a result of exchange the phase shifts $\delta_1^\pm$ and $\delta_2^\pm$ are much greater than the values $\delta_1$ and $\delta_2$ which are obtained without allowing for the exchange. Figure 20 shows the total elastic scattering cross-section (or more precisely the sum of the three first partial cross-sections). The various experimental points are given for comparison [45].

*Chapter 5*

# EXCITATION OF THE HYDROGEN ATOM BY ELECTRON IMPACT

## 18. Approximate Method for the Calculation of the Effective Excitation Cross-section

The various approximate methods can conveniently be discussed on the basis of the system of equations given by (10.55). If we confine our attention to direct transitions between the initial and final states and neglect virtual transitions to intermediate states and also the coupling between different real transitions in the case of multichannel processes, then the system given by (10.55) reduces to the following two equations:

$$\Delta F_\alpha + (k_\alpha^2 - 2V_{\alpha\alpha})F_\alpha - 2\int W_{\alpha\alpha} F_\alpha \, dr' = 2V_{\alpha 0} F_0 + 2\int W_{\alpha 0} F_0 \, dr' \qquad (18.1)$$

$$\Delta F_0 + (k_0^2 - 2V_{00})F_0 - 2\int W_{00} F_0 \, dr' = 2\left(V_{0\alpha} F_\alpha + \int W_{0\alpha} F_\alpha \, dr'\right) \qquad (18.2)$$

The quantities $V_{\alpha\alpha}$, $W_{\alpha\alpha}$, $V_{00}$, $W_{00}$ and $W_{\alpha 0}$ fall off exponentially as $r \to \infty$. The quantity $V_{\alpha 0}$ falls off as $r^{-l-1}$ when $r \to \infty$ (except in the case of transitions between $s$-states when $V_{\alpha 0}$ is also found to be exponential). If we retain only the slowly decreasing interactions represented by $V_{\alpha 0}$ and neglect all others we obtain

$$\Delta F_\alpha + k_\alpha^2 F_\alpha = 2V_{\alpha 0} F_0 \qquad (18.3)$$

$$\Delta F_0 + k_0^2 F_0 = 2V_{0\alpha} F_\alpha \qquad (18.4)$$

The simplest and crudest approximation is the Born approximation in which $V_{0\alpha}$ is regarded as a small perturbation. The term $V_{0\alpha}F_\alpha$ on the right-hand side of (18.4) is then neglected and a plane wave is substituted for $F_0$ on the right-hand side of (18.3). As a result we have†

$$\Delta F_\alpha + k_\alpha^2 F_\alpha = 2V_{\alpha 0} e^{ik_0 v.r} \qquad (18.5)$$

The amplitude $q_\alpha$ on the Born approximation is

$$q_{0\alpha} = -\frac{1}{2\pi}\int e^{-i(k_\alpha n - k_0 v)r'} V_{\alpha 0} \, dr' \qquad (18.6)$$

---

† There exists also the so-called Born-Oppenheimer approximation in which (18.5) is augmented by the exchange term $\int W_{\alpha 0} e^{ik_0 v.r'} dr'$ where the function $F_0$ is replaced by a plane wave. However, numerical calculations have shown that this leads to a considerable overestimate of the cross-section. In many cases the cross-section calculated on this approximation exceeds the theoretical limit by a large factor. A modification which removes much of the discrepancy is described in [105].

Let us introduce the vector

$$K = k_\alpha n - k_0 v \tag{18.7}$$

which represents the momentum transfer. In this notation we have

$$q_{0\alpha} = -\frac{1}{2\pi}\int e^{-iK.r}\, V_{\alpha 0}\, dr \tag{18.8}$$

We can now use the expression for $V_{\alpha\alpha'}$ given by (10.20) to transform (18.8) to the form (cf (5.25))

$$q_{0\alpha} = \frac{2}{K^2}\int e^{-iK.r}\,\psi_\alpha^*\psi_0\, dr = \frac{2}{K^2}(e^{-iK.r})_{\alpha 0} \tag{18.9}$$

The total excitation cross-section is given by

$$\sigma_{0\alpha} = 2\pi\frac{k_\alpha}{k_0}\int_0^\pi |q_\alpha|^2 \sin\theta\, d\theta$$

The integration with respect to $\theta$ may be replaced by integration with respect to $K$. From (18.2) we have

$$K^2 = k_\alpha^2 + k_0^2 - 2k_\alpha k_0 \cos\theta \tag{18.10}$$

Since

$$k_\alpha^2 = k_0^2 - 2\Delta E \tag{18.11}$$

where

$$\Delta E = E_\alpha - E_0 \tag{18.12}$$

it follows that

$$K^2 = 2(\Delta E - k_\alpha k_0 \cos\theta) \tag{18.13}$$

and hence

$$K\, dK = k_0 k_\alpha \sin\theta\, d\theta \tag{18.14}$$

Therefore,

$$\sigma_{0\alpha} = \frac{8\pi}{k_0^2}\int_{k_0 - k_\alpha}^{k_0 + k_\alpha} |(e^{-iK.r})_{\alpha 0}|^2 \frac{dK}{K^3} \tag{18.15}$$

When the momentum transfer is small, the matrix element $(e^{iK.r})_{\alpha 0}$ can be expanded into a series in powers of $K$. The first term will vanish because the wave functions of the excited and ground states of the atom are orthogonal. For optically allowed transitions $(e^{iK.r})_{\alpha 0} \approx K(r)_{\alpha 0}$, which may be referred to as the dipole approximation. The quantity $(r)_{\alpha 0}$ in its turn is related to the oscillator strength for the transition $0 \rightarrow \alpha$ [56]. In general, the dipole approximation for $(e^{iK.r})_{\alpha 0}$ cannot be used in the entire range of integration in (18.15) since at the upper limit the quantity $K$ may not, in fact, be small [57]. However, the expression given by (18.15) may be modified by introducing instead of the upper limit $k_0 + k_\alpha$, an effective number $k'$ which is chosen so that the dipole approximation can be used in the entire range of integration. The number $k'$ can, for example, be determined from the condition that for sufficiently high energies the magnitude of the cross-section $\sigma$ calculated from (18.15) (without expansion in the powers of $K$) should be practically identical with the value of $\sigma$ calculated on the dipole approximation [58]. On substituting the dipole approximation for $(e^{i\mathbf{K}\cdot\mathbf{r}})_{\alpha 0}$ into (18.15) we have

$$\sigma_{0\alpha} = \frac{8\pi}{k_0^2}(r)_{\alpha 0}^2 \ln \frac{k'}{k_0 - k_\alpha} \tag{18.16}$$

Since, on the dipole approximation, the cross-section $\sigma$ is a logarithmic function of $k'$, the latter need not be determined to a high degree of accuracy. On the dipole approximation, therefore, the excitation cross-section $\sigma_{0\alpha}$ can be expressed in terms of the oscillator strength.

On the Born approximation the expression for the partial amplitude is obtained with the aid of the partial-wave expansion (18.8). On the total angular momentum representation we then have

$$q_{\nu\nu'} = -2\int_0^\infty u_{l_2}(k_0 r)\mathscr{V}_{\nu\nu' L} u_{l_2'}(k_\nu r)\, dr \tag{18.17}$$

We note that even at low energies (near the threshold), the amplitude (18.17) for a given transition is not a monotonically decreasing function of the angular momentum $l_2$ of the incident electron. In contrast to elastic scattering, when the $s$-wave has a dominating effect at low energies while the contribution due to partial waves with $l \neq 0$ is small and decreases rapidly with $l$, it turns out that in the present case the dominant partial wave is that corresponding to a value of $l_2$ which is not the smallest value. This phenomenon was established, for example, in [56] as a result of calculations of the excitation of $p$-levels in He. The reason why a partial wave corresponding to an angular momentum $l_2$ may give a bigger contribution than waves with $l_2 - 1$ and $l_2 + 1$ can be deduced by analysing the properties of the integrand in (18.17). For example, when the atom undergoes a transition from the $s$-state to the $p$-state, the matrix element $\mathscr{V}_{\nu\nu' L}$ vanishes at $r = 0$ and $r \to \infty$, while its modulus $|\mathscr{V}_{\nu\nu' L}|$ has a maximum for $r$ of the order of a few atomic units of length. The functions $u_{l_2}$ and $u_{l_2'}$ vanish at $r = 0$ and then monotonically increase with increasing $r$ up to the first extremum (the position of the extremum depends on $l_2$ and $k$). As $r$ is increased still further, the two functions exhibit an oscillatory behaviour. At $r = 0$, and in the oscillatory region, $u_{l_2}$ and $u_{l_2'}$ contribute very little to the integral. In order that the value of the integral as a whole should be sufficiently large, it is necessary that the first maxima of $u_{l_2}$ and $u_{l_2'}$ should lie in the neighbourhood of the maximum of $|\mathscr{V}_{\nu\nu' L}|$. This is achieved only at a particular optimum value of $l_2$.

A modification of the Born approximation has been given in [59]. In this work the idea was to calculate the reaction matrix K given by (12.11) on the Born approximation, i.e. assume that

$$\mathrm{K} = -\mathrm{k}^{l+\frac{1}{2}}\mathrm{B}_0\mathrm{k}^{l+\frac{1}{2}} \tag{18.18}$$

where $B_0$ is obtained from B by replacing the functions $x_{\gamma'\gamma''}$ in (10.72) by the terms $u_{\gamma'}\delta_{\gamma'\gamma''}$ outside the integral. The exchange interaction was neglected. We shall denote the approximate reaction matrix given by (18.18) by $K^{(0)}$ and the approximate amplitude by $q^{(0)}$. According to (12.9):

$$q^{(0)} = k^{-\frac{1}{2}}K^{(0)}(1-iK^{(0)})^{-1}k^{-\frac{1}{2}} \tag{18.19}$$

In point of fact this approximation is a generalization of the formula given by (5.18) which was derived for elastic scattering by a centre of force. If the matrix elements of $K^{(0)}$ are small, then $q^{(0)} \approx k^{-\frac{1}{2}}K^{(0)}k^{-\frac{1}{2}}$ and we have the Born approximation. However, if the interaction is sufficiently strong, the Born amplitude given by (18.17) may exceed the limit set by the unitarity relation for the accurate amplitude, while the expression given by (18.19) will never exceed this limit. Therefore, the latter expression may be looked upon as a reasonable extrapolation of the Born approximation to the region of strong interaction. It may be used to allow, at least in part, for the effect of coupling of the type $a \to a'$, $a \to a' \to a''$ and also the competition between the $a \to a'$ and $a \to a''$ transitions. In this method it is no longer possible to sum over all the partial waves by reducing the entire sum to a simple expression of the form of (18.8) as on the Born method. However, in some cases it is sufficient to take into account a few partial waves, and then the summation problem does not arise. When a large number of partial waves enter into the calculations it is occasionally possible to use the fact that, beginning with a certain value $l_0$, the amplitude calculated from (18.19) is practically identical with that found on the Born approximation. We then have the approximate relation

$$\sigma = \sigma^B + \sum_{l=0}^{l_0}(\sigma_l - \sigma_l^B)$$

When $l_0$ is very large, this method is not particularly productive and other methods of estimating this part of the sum must be found. In [60] the specific case of the excitation of the hydrogen atom is used to discuss in detail the various possible methods of summing over all the partial waves.

The effect of the atomic field and the exchange interaction on the electron can be calculated on the distorted wave approximation. In this method, the quantities $V_{\alpha\alpha}$, $W_{\alpha\alpha}$, $V_{00}$ and $W_{00}$ are retained in the system given by (18.1) and (18.2). Moreover, $V_{\alpha 0}$ and $W_{\alpha 0}$ are retained in (18.1), but in (18.2) they are neglected. In this way one obtains the uncoupled equations

$$\Delta F_\alpha + (k_\alpha^2 - 2V_{\alpha\alpha})F_\alpha - 2\int W_{\alpha\alpha}F_\alpha\, d\mathbf{r}' = 2V_{\alpha 0}F_0 + 2\int W_{\alpha 0}F_0\, d\mathbf{r}' \tag{18.20}$$

$$\Delta F_0 + (k_0^2 - 2V_{00})F_0 - 2\int W_{00}F_0\, d\mathbf{r}' = 0 \tag{18.21}$$

The asymptotic forms of $F_\alpha$ and $F_0$ are

$$\left.\begin{aligned} F_0 &= e^{ik_0\mathbf{v}\cdot\mathbf{r}} + q_0\frac{e^{ik_0 r}}{r} \\ F_\alpha &= q_{0\alpha}\frac{e^{ik_\alpha r}}{r} \end{aligned}\right\} \tag{18.22}$$

Let $G_\alpha(r, r')$ be the Green's function satisfying the equation

$$\Delta G_\alpha + (k_\alpha^2 - 2V_{\alpha\alpha})G_\alpha - 2\int W_{\alpha\alpha}(r, r'')G_\alpha(r'', r')\,dr'' = \delta(r' - r) \tag{18.23}$$

and having the following asymptotic form for $r \to \infty$

$$G_\alpha \sim \frac{1}{4\pi}\frac{e^{ik_\alpha r}}{r}\mathscr{F}_\alpha(r') \tag{18.24}$$

where $\mathscr{F}_\alpha$ is a function to be determined. We can then write

$$F_\alpha = -2\int G(r, r')\left(V_{\alpha 0}F_0 + \int W_{\alpha 0}F_0\,dr''\right)dr' \tag{18.25}$$

In view of (18.24) we have for large $r$

$$F_\alpha \sim -\frac{1}{2\pi}\frac{e^{ik_\alpha r}}{r}\int \mathscr{F}_\alpha\left(V_{\alpha 0}F_0 + \int W_{\alpha 0}F_0\,dr''\right)dr' \tag{18.26}$$

and hence

$$q_{0\alpha} = -\frac{1}{2\pi}\int \mathscr{F}_\alpha\left(V_{\alpha 0}F_0 + \int W_{\alpha 0}F_0\,dr''\right)dr' \tag{18.27}$$

In order to elucidate the significance of the function $\mathscr{F}_\alpha$ let us express $G$ in terms of $G_0$, which is given by

$$G_0 = -\frac{1}{2\pi}\frac{e^{ik_\alpha|r-r'|}}{|r-r'|} \tag{18.28}$$

The connection between $G$ and $G_0$ is contained in the integral equation

$$G = G_0 - \int V_{\alpha\alpha}(r'')G(r, r'')G_0(r'', r')\,dr''$$
$$-\int W_{\alpha\alpha}(r'', r''')G(r, r''')G_0(r'', r')\,dr''\,dr''' \tag{18.29}$$

For large $r$

$$G_0 \sim -\frac{1}{4\pi}\frac{e^{ik_\alpha r}}{r}e^{-ik_\alpha n . r'} \tag{18.30}$$

Assuming that, for large $r$, $G$ is given by (18.24) we have

$$\mathscr{F}_\alpha(r) = e^{-ik_\alpha n . r'} - 2\int V_{\alpha\alpha}G_0\mathscr{F}\,dr' - 2\int WG_0\mathscr{F}\,dr'dr'' \tag{18.31}$$

We thus obtain an integral equation which is equivalent to the integro-differential equation

$$\Delta\mathscr{F}_\alpha + (k_\alpha^2 - 2V_{\alpha\alpha})\mathscr{F}_\alpha - 2\int W_{\alpha\alpha}\mathscr{F}_\alpha\,dr = 0 \tag{18.32}$$

with the asymptotic behaviour

$$\mathscr{F}_\alpha \sim e^{-ik_\alpha nr} + Q_{\alpha\alpha}\frac{e^{ik_\alpha r}}{r} \tag{18.33}$$

As can be seen from these formulae the function $\mathscr{F}$ describes the elastic scattering of an electron by the excited atom where prior to the collision the electron has the momentum $k_\alpha n$. The distorted wave method involves the resolution of $F$ and $\mathscr{F}$ into partial waves. The partial amplitude $q_{vv'}$ in the distorted wave approximation is proportional to the integral

$$\int_0^\infty f_{v,L}(r)\left[\mathscr{V}_{v,v'L}(r)f_{v',L}(r)+\int_0^\infty \mathscr{W}_{v,v'L}(r',r)f_{v',L}(r')\,dr'\right]dr$$

where $f_{v',L}$ describes the elastic scattering with angular momentum $l_2'$ by an atom in the ground state, where $f_{v,L}$ represents the elastic scattering with angular momentum $l_2$ by an excited atom in the state $n$, $l_1$. As in the simplest case of the Born approximation, $q_{vv'}$ is not a monotonic function of the angular momentum $l_2$ of the incident electron. There are special values of $l_2$ which play a dominant role. These values are somewhat different from those which enter into the Born approximation, since the zeros and the extrema of the functions $f_{v,L}$ are displaced relative to the corresponding points for the functions $u_{l_2}(r)$.

One occasionally uses a simplified version of the distorted wave approximation in which the exchange interaction is neglected, so that (18.20) and (18.21) are replaced by

$$\begin{aligned}\Delta F_\alpha+(k_\alpha^2-2V_{\alpha\alpha})F_\alpha&=2V_{\alpha 0}F_0\\ \Delta F_0+(k^2-2V_{00})F_0&=0\end{aligned}\qquad(18.34)$$

We note that unless factors other than the distortion are also taken into account (for example, exchange and coupling through intermediate states), the final result may not in fact constitute an improvement on the Born approximation, but may on the contrary lead to an even larger discrepancy between the approximate and true amplitudes.

A review of the various versions of these methods from the point of view of variational principles is given in [17].

When all the terms in (18.1)–(18.2) are included, the corresponding approximation is known as the strong coupling approximation. However, this approximation takes into account only the strong coupling $0-\alpha$ and ignores the effect of $0-\alpha'-\alpha''$ etc. coupling. Nevertheless, the effect of the latter may be appreciable, so that it is better to consider a system of a number of equations which take into account the coupling within a group of states. Both the distorted wave and the strong coupling approximation involve extensive numerical work which is usually carried out by computers. A detailed discussion of the various problems associated with the selection of the best computational scheme is given in [61].

In addition to numerical calculations, use can also be made of variational methods. In their simplest form the variational methods are employed within the framework of the distorted wave approximation. As was shown above, in the distorted wave approximation the transition amplitude is expressed in terms of functions describing elastic scattering by the atom in the ground and excited states. These functions may be represented by approximate analytic functions containing parameters to be varied. Therefore, the application of the variational method reduces to the determination of the optimum parameters of trial functions describing elastic scattering—a problem with which we are already familiar [17]. If the excited state is an $s$-state, the trial function will in general have the same structure as in the case of elastic scattering in the ground state. But if the excited state has a non-zero angular momentum, then the variational calculation becomes so involved that it is much easier to carry out a numerical integration of the equation.

The application of variational methods becomes more difficult in the case of the strong coupling approximation. Comparisons of different methods, and also the comparison of variational calculations with the exact solution (using a model which admits of an analytical solution on the strong coupling approximation) are given in [62].

Below we give the results of some calculations concerned with the excitation of the hydrogen atom to different states; these will be compared with experimental results.

## 19. EXCITATION OF THE 2s-STATE

The excitation of the $2s$-state of the hydrogen atom has been extensively investigated. It is the testing ground for the various methods which are available for such calculations. Thus, calculations have been carried out using the modified Born approximation [60], the distorted wave approximation [63], the strong coupling approximation ($1s-2s$) [64], and finally calculations with allowance for the $1s-2s-2p$ coupling [61, 65].

It is evident from Table 1 that the latter calculation involves the solution of three equations for $L = 0$ and four equations for each of the angular momenta $L > 0$. The calculations yield the excitation cross-section for the $2s$-state and for the $2p$-state. Partial cross-sections for $0 \leqslant L \leqslant 4$ are calculated in [65] and for $0 \leqslant L \leqslant 6$ in [61]. The total cross-section can be obtained by adding the partial cross-sections for large $L$, calculated on the modified Born approximation. Figure 21, which is based on the data reported in [65], shows the excitation cross-section for the $2s$-state averaged over the spins and computed on different approximations. The partial cross-sections for angular momenta $L$ between 0 and 2 are shown separately for the triplet and singlet states in Fig. 22. Inspection of these figures shows that the results obtained when the $1s-2s$ coupling is taken into account are not very different from those obtained when $1s-2s-2p$ coupling is allowed for. The addition of the $2p$ coupling has little effect on the excitation cross-section in the triplet state, except for the region near the threshold; but it has a more pronounced effect in the singlet state. Moreover, the cross-section near threshold is increased when $2p$ is taken into account, whereas away from the threshold it is reduced. The partial cross-sections for large $L$ exhibit a greater relative change when the coupling with $2p$ is added than do the cross-sections corresponding to small $L$.

The excitation cross-section for the $2s$-state has been determined experimentally [66]. Direct measurements of the $1s-2s$ transition cross-section

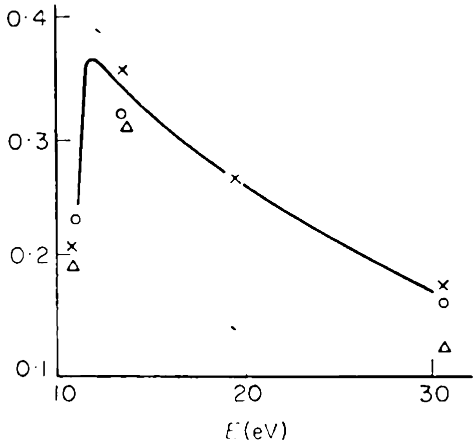


FIG. 21. Cross-section for the excitation of the $2s$-state (in units of $\pi a_0{}^2$): solid curves—distorted wave approximation (sum of partial cross-sections for $L = 0, 1, 2$); crosses—with $1s - 2s - 2p$ coupling (all partial waves); open circles—strong $1s - 2s$ coupling approximation (sum over $L = 0, 1, 2$); triangles—with $1s - 2s - 2p$ coupling (sum over $L = 0, 1, 2$)

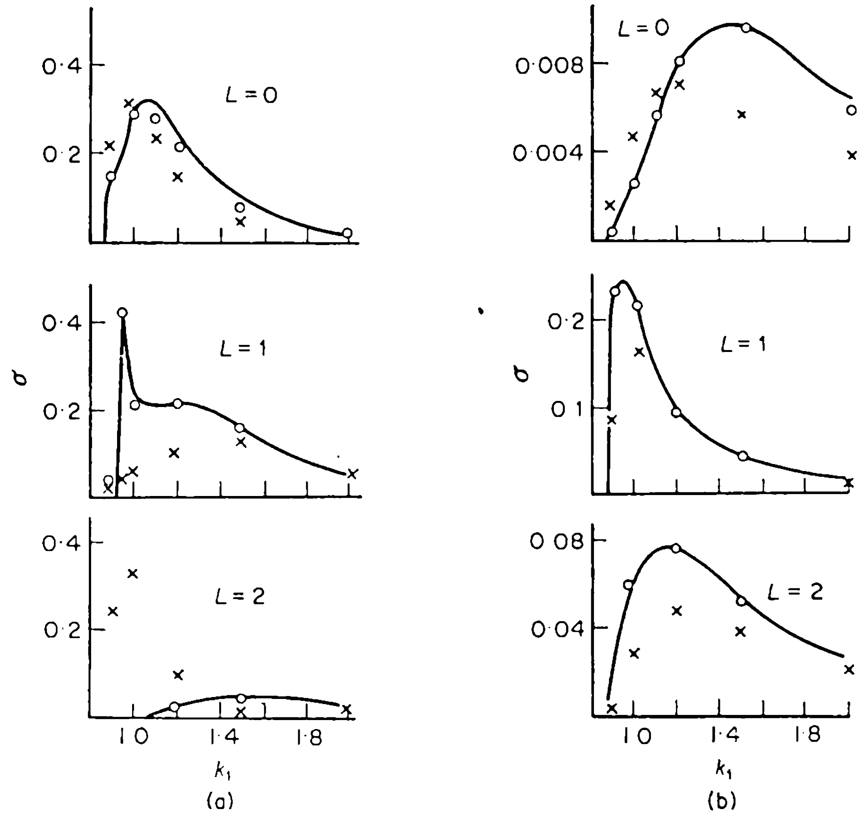


FIG. 22. Partial cross-sections for the excitation of the $2s$-state in units of $\pi a_0{}^2$: ($a$)—symmetric case, ($b$)—antisymmetric case (solid curves—distorted wave approximation; open circles—with strong $1s - 2s$ coupling; crosses—with $1s - 2s - 2p$ coupling)

are not readily obtainable, and therefore in the experiment metastable hydrogen atoms in the 2*s*-state were subjected to the action of an electric field which induced their transitions to the 2*p*-state. The radiation due to the $2p-1s$ transition was measured, and from the intensity of this radiation an estimate was made of the magnitude of $\sigma(1s-2p)$. In order to obtain the absolute magnitude of $\sigma$ it was necessary to introduce a calibration. For example, it was assumed in [66] that at 45 eV the cross-section $\sigma$ is practically equal to the cross-section obtained on the Born approximation. Another method of calibration was used in [67].

The results reported in [66] and [67] differ by a factor of about 2. The reason for the discrepancy is obscure, and therefore the comparison between theory and experiment is somewhat preliminary in nature. Nevertheless, there is a good agreement between the calculations of [65] and the experiment described in [66]. Figure 23 shows the experimental curve and the theoretical results from [65].

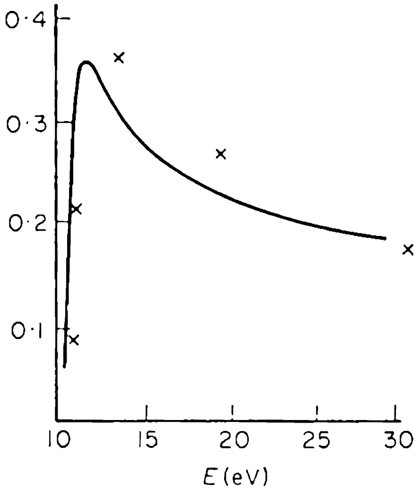


FIG. 23. Calculated cross-sections for the excitation of the 2*s*-state and experimental results (solid curve—experimental; crosses—calculation including $1s - 2s - 2p$ coupling. The cross-section is given in units of $\pi a_0^2$

## 20. EXCITATION OF THE 2*p*-STATE

The cross-section for the excitation of the 2*p*-state has been calculated on the Born approximation [60] by the distorted wave method [68] and with allowance for the $1s-2s-2p$ coupling [65]. As in the calculation of the excitation of the 2*s*-state, the partial cross-sections with allowance for the $1s-2s-2p$ coupling were determined for $0 \leqslant L \leqslant 6$ and were then augmented by the cross-sections calculated on the Born approximation for $L > 6$.

Figure 24 shows the partial cross-sections for $L = 0, 1, 2$ calculated by different methods. The formula given by (11.13) was used to determine the amplitudes for the excitation of the $2p_0$ and $2p_{\pm 1}$ states. The excitation

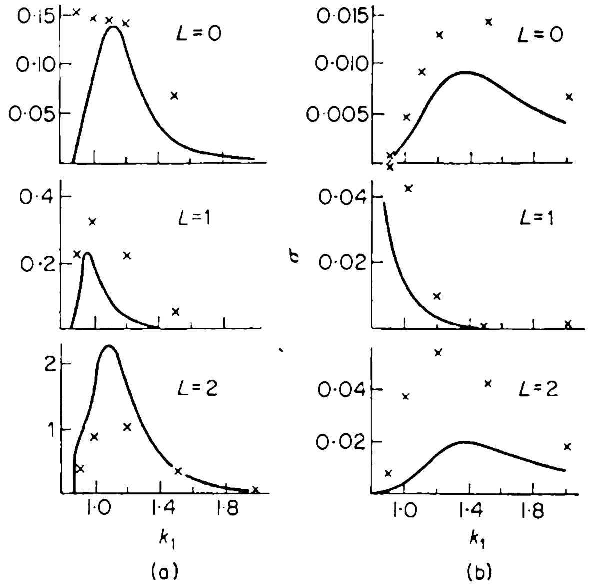


FIG. 24. Partial cross-sections for the excitation of the $2p$-state (in units of $\pi a_0^2$): (*a*) symmetric case, (*b*) antisymmetric case (solid curves—distorted wave approximation; open circles—with strong coupling $1s - 2s$; crosses—calculation with coupling. For $L = 1, 2$, the cross-sections are reduced, taking $l_2 = L - 1$)

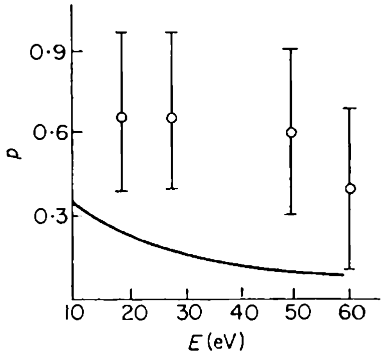


FIG. 25. Polarization of the radiation emitted as a result of the $2p \rightarrow 1s$ transition (curve — calculations; points — experimental)

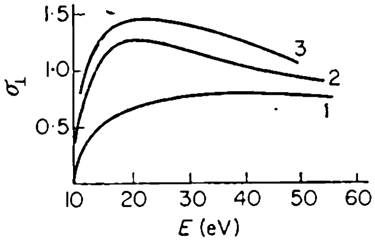


FIG. 26. Comparison of measured and calculated values for $\sigma_\perp$: 1—experiment; 2—calculated with $1s - 2s - 2p$ coupling; 3—Born approximation (all in units of $\pi a_0^2$)

cross-sections for these states, $\sigma(2p_1)$ and $\sigma(2p_0)$, were then calculated from these amplitudes. In addition the following quantities were calculated:

1. The total cross-section for the excitation of the $2p$-state:

$$\sigma(2p) = \sigma(2p_0) + 2\sigma(2p_1) \tag{20.1}$$

2. The cross-section $\sigma_\perp$ determined experimentally from the number of photons emitted by the excited atoms in the direction perpendicular to the direction of the electron beam. This cross-section is given [69] by:

$$\sigma_\perp = 0{\cdot}918\sigma(2p_1) + 0{\cdot}246\sigma(2p_0) \tag{20.2}$$

3. The polarization of the radiation emitted at right angles to the direction of the electron beam [69]:

$$P = 3\left[1-\frac{\sigma(2p_1)}{\sigma(2p_0)}\right]\frac{1}{7+11\dfrac{\sigma(2p_1)}{\sigma(2p_0)}} \tag{20.3}$$

The calculated cross-sections are given in Table 5 in units of $\pi a_0^2$. The calculated values of $P$ and $\sigma$ are compared with experimental values in Figs. 25 and 26.

TABLE 5

| $k$ | $\sigma(2p_1)$ | $\sigma(2p_0)$ | $\sigma(2p)$ | $\sigma_\perp$ | $P$ |
|---|---|---|---|---|---|
| 0·9 | 0·0683 | 0·2234 | 0·3599 | 0·3853 | 0·2009 |
| 1 | 0·0997 | 0·6005 | 0·7909 | 0·8820 | 0·2835 |
| 1·1 | 0·1395 | 0·8149 | 1·0939 | 1·2047 | 0·2799 |
| 1·2 | 0·1631 | 0·8539 | 1·1801 | 1·2934 | 0·2667 |
| 1·5 | 0·2244 | 0·6423 | 1·0911 | 1·1596 | 0·1800 |
| 2 | 0·2395 | 0·3927 | 0·8716 | 0·8968 | 0·0855 |

## 21. EXCITATION OF STATES WITH $n \geqslant 2$

The excitation of states with $n = 2$, 3 and 4 has been calculated on the Born approximation in [70]. The effective cross-sections summed over $l$ and $\mu$ for given $n$ are given in Table 6.

TABLE 6

| $E$ (eV) | Cross-sections (in units of $\pi a_0^2$) for the transitions | | | | |
|---|---|---|---|---|---|
| | 1—2 | 1—3 | 1—4 | 1—5 | 1—6 |
| 13·5 | 1·2818 | 0·1787 | 0·0509 | 0·0202 | 0·0092 |
| 19·5 | 1·5354 | 0·2782 | 0·0999 | 0·0476 | 0·0265 |
| 26·5 | 1·4993 | 0·2798 | 0·1021 | 0·0490 | 0·0274 |
| 34·8 | 1·3886 | 0·2600 | 0·0951 | 0·0457 | 0·0256 |

The interpolation method was used to determine the excitation cross-sections for states with $n = 5$ and $n = 6$. This method is based on the fact that for large quantum numbers $n$ an energy change of $dE$ is related to the change $dn$ in the quantum number by

$$dn \sim n^3\, dE \tag{21.1}$$

The excitation cross-section of an atom in the interval $dn$ near $n$ is

$$d\sigma = \sigma_n \, dn \qquad (21.2$$

or, on substituting (21.1)

$$d\sigma = \sigma_n n^3 \, dE \qquad (21.3)$$

In the case of ionization of the atom, the probability that the ejected electron will be found in an energy interval $d\varepsilon$ may be written in the form

$$d\sigma = \sigma_\varepsilon \, d\varepsilon \qquad (21.4)$$

It is therefore expected that $n^3\sigma_n$ will be a continuous function of $n$ which goes smoothly into $\sigma_\varepsilon$ when $n \to \infty$.` Figure 27 shows $n^3\sigma_n$ as a function of the energy of the atomic electron. Negative values correspond to discrete levels, positive values to ionization. In the region of ionization, $\sigma_\varepsilon$ was calculated on the Born approximation. The broken curves indicate the interpolation region. The excitation cross-sections calculated in this way for states with $n = 5$ and $n = 6$ are also given in Table 6, but we only cover the low energy region. In [70] the cross-sections are calculated up to energies of about 1000 eV.

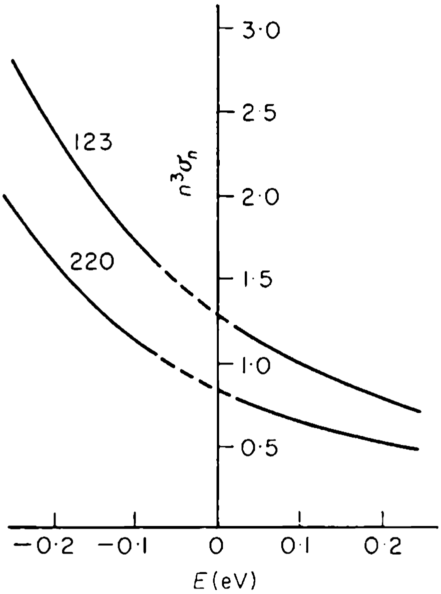


FIG. 27. Dependence of $n^3\sigma_n$ on the energy of the atomic electron ($\sigma$ in units of $\pi a_0^2$). The figures against the curves indicate the energy of the incident electron in eV)

## 22. TRANSITIONS OF AN EXCITED ATOM INTO HIGHER LEVELS AS A RESULT OF A COLLISION WITH AN ELECTRON

In the preceding sections we considered transitions of an atom from the ground to the excited state produced by electron impact. In some cases it is necessary to know the cross-sections for the excitation of atoms from excited states to higher excited states. A number of such transitions have been treated on the Born approximation.

The cross-section for the transition from the $2s$-state to all the levels with $n$ between 3 and 10 summed over $l$ and $\mu$ are calculated in [71]. The calculations were based on the general formula for values of $n$ up to $n = 7$, whereas for $n = 8$, 9 and 10 use was made of the interpolation method described in § 21 in connection with the $1s-n$ transition. The calculations in [71] are concerned with the energy range between 4·85 and 120 eV. Some of the results are given in Table 7. As is expected, the calculated cross-sections are much greater than the cross-sections for the corresponding transitions from the ground state.

TABLE 7

| $E$ (eV) | Cross-sections (in units of $\pi a_0^2$) for the transitions | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $2s-3$ | $2s-4$ | $2s-5$ | $2s-6$ | $2s-7$ | $2s-8$ | $2s-9$ | $2s-10$ |
| 4·85 | 65·019 | 12·330 | 4·658 | 2·312 | 1·331 | 0·843 | 0·569 | 0·404 |
| 8·65 | 49·441 | 9·454 | 3·612 | 1·808 | 1·047 | 0·664 | 0·450 | 0·320 |
| 13·5 | 37·667 | 7·150 | 2·726 | 1·364 | 0·790 | 0·499 | 0·339 | 0·241 |
| 26·4 | 23·703 | 4·446 | 1·687 | 0·842 | 0·487 | 0·309 | 0·209 | 0·149 |
| 34·6 | 19·488 | 3·640 | 1·379 | 0·687 | 0·397 | 0·252 | 0·170 | 0·121 |

Transitions from the $2p_0$ and $2p_{\pm 1}$ states to levels with $n$ between 3 and 10 were calculated using an analogous method in [72] in the energy range between 4·85 and about 120 eV. Some of the results are given in Tables 8a and 8b. It is possible to use these data to determine the excitation cross-section from the $2p$-state averaged over $\mu$:

$$\sigma(2p) = \tfrac{1}{3}\sigma(2p_0)+\tfrac{2}{3}\sigma(2p_{\pm 1}) \tag{22.1}$$

TABLE 8A

| $E$ (eV) | Cross-sections (in units of $\pi a_0^2$) for the transitions | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $2p_0-3$ | $2p_0-4$ | $2p_0-5$ | $2p_0-6$ | $2p_0-7$ | $2p_0-8$ | $2p_0-9$ | $2p_0-10$ |
| 4·85 | 74·837 | 14·426 | 5·259 | 2·499 | 1·409 | 0·892 | 0·601 | 0·424 |
| 8·65 | 64·529 | 12·323 | 4·749 | 2·347 | 1·348 | 0·861 | 0·586 | 0·417 |
| 13·5 | 52·482 | 9·826 | 3·790 | 1·859 | 1·072 | 0·684 | 0·461 | 0·328 |
| 26·4 | 35·403 | 6·352 | 2·408 | 1·176 | 0·677 | 0·432 | 0·288 | 0·207 |
| 34·6 | 29·727 | 5·246 | 1·974 | 0·963 | 0·553 | 0·348 | 0·234 | 0·165 |

TABLE 8B

| $E$ (eV) | Cross-sections (in units of $\pi a_0^2$) for the transitions | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $2p_1 - 3$ | $2p_1 - 4$ | $2p_1 - 5$ | $2p_1 - 6$ | $2p_1 - 7$ | $2p_1 - 8$ | $2p_1 - 9$ | $2p_1 - 10$ |
| 4·85 | 76·515 | 13·346 | 4·995 | 2·512 | 1·414 | 0·890 | 0·600 | 0·424 |
| 8·65 | 57·44 | 10·692 | 4·052 | 2·040 | 1·166 | 0·740 | 0·505 | 0·358 |
| 13·5 | 45·05 | 8·181 | 3·077 | 1·537 | 0·883 | 0·560 | 0·378 | 0·270 |
| 26·4 | 29·278 | 5·102 | 1·891 | 0·935 | 0·537 | 0·342 | 0·229 | 0·160 |
| 34·6 | 24·313 | 4·173 | 1·538 | 0·758 | 0·435 | 0·268 | 0·180 | 0·128 |

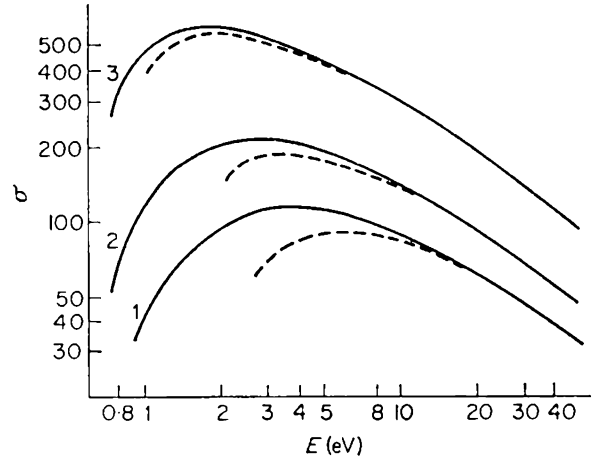


FIG. 28. Cross-sections for the transitions $3s - 4p$ (curve 1), $3p - 4d$ (curve 2) and $3d - 4f$ (curve 3). The cross-sections are given in units of $\pi a_0^2$

The cross-sections for the following transitions were calculated in a number of papers [73, 74, 75] (see Figs. 28–34)†:

$$3s \rightarrow (4s, 4p, 4d, 4f, 5p)$$
$$3p \rightarrow (4s, 4p, 4d, 4f, 5d)$$
$$3d \rightarrow (4s, 4p, 4d, 4f, 5f)$$
$$4s \rightarrow (5p, 6p)$$
$$4p \rightarrow 5d$$
$$4d \rightarrow 5f$$
$$4f \rightarrow (5g, 6g)$$
$$5(s, p, d, f, g) \rightarrow 6(p, d, f, g, h)$$

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† The broken curves in these figures represent the dipole approximation.

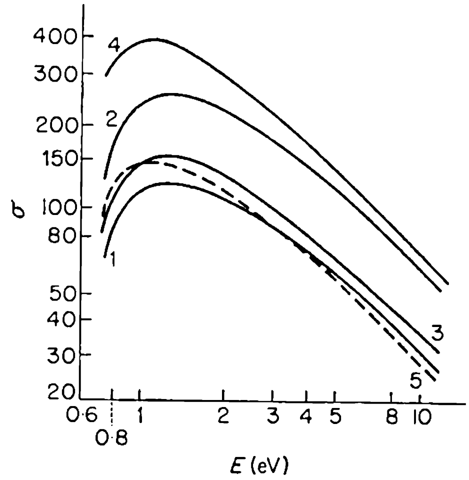

FIG. 29. Cross-sections for the transitions $3s - 4s$ (curve 1), $4s - 4d$ (curve 2), $3p - 4p$ (curve 3), $3p - 4f$ (curve 4), and $3d - 4d$ (curve 5). The cross-sections are given in units of $\pi a_0^2$

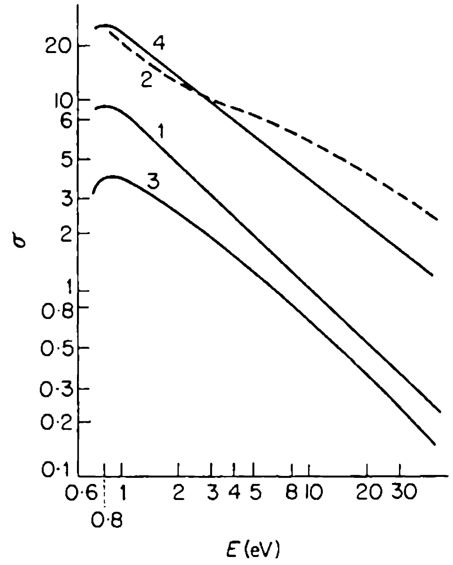

FIG. 30. The cross-sections (in units of $\pi a_0^2$) for the transitions $3s - 4f$ (curve 1), $3p - 4s$ (curve 2), $3d - 4s$ (curve 3), and $3d - 4d$ (curve 4). The scale for curve 1 is reduced by a factor of 30

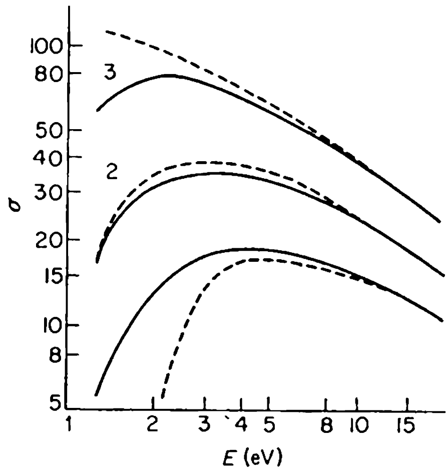

FIG. 31. The cross-sections (in units of $\pi a_0^2$) for the transitions $3s - 5p$ (curve 1), $3p - 5d$ (curve 2), and $3d - 5f$ (curve 3)

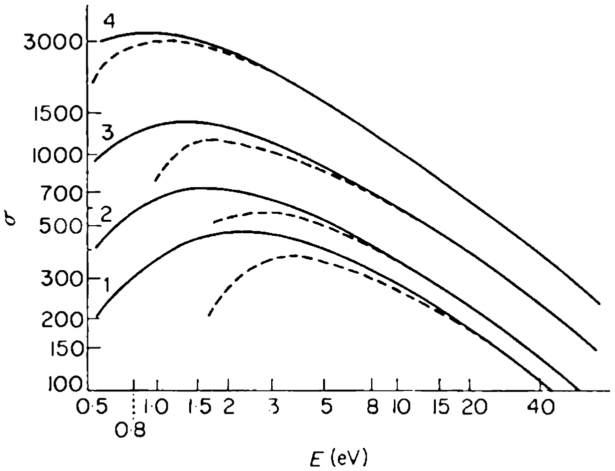

FIG. 32. Cross-sections for the transitions $4s - 5f$ (curve 1), $4p - 5d$ (curve 5), $4d - 5f$ (curve 3), and $4f - 5g$ (curve 4). The cross-sections are given in units of $\pi a_0^2$

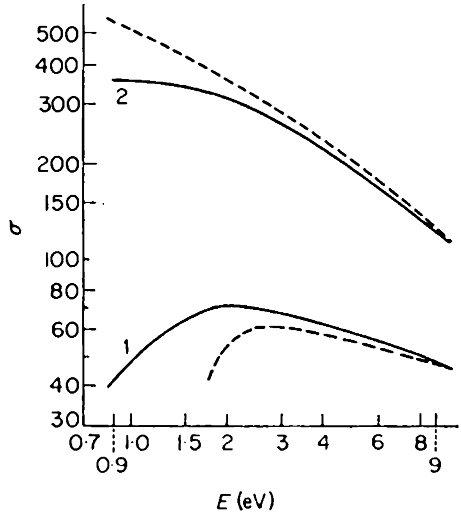

FIG. 33. Cross-sections for the transitions $4s - 6p$ (curve 1), and $4f - 6g$ (curve 2). The cross-sections are given in units of $\pi a_0^2$

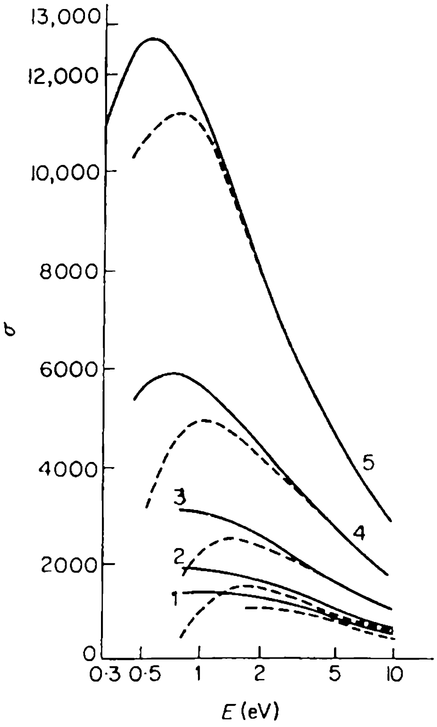

FIG. 34. Cross-sections for the transitions $5s - 6p$ (curve 1), $5p - 6d$ (curve 2), $5d - 6f$ (curve 3), $5f - 6g$ (curve 4), and $5g - 6h$ (curve 5). The cross-sections are given in units of $\pi a_0^2$

As can be seen from Figs. 28–34, the cross-sections for these transitions are much greater than the cross-sections for the corresponding transitions from the ground state. The cross-sections for optically allowed transitions involving an increase in $l$ are greater than the cross-sections for optically allowed transitions involving a decrease in $l$.

## *Chapter 6*

# THE COLLISION OF AN ELECTRON WITH A HELIUM ION

### 23. THE ELASTIC SCATTERING OF AN ELECTRON BY A HELIUM ION AND THE EXCITATION OF THE 2*s* STATE OF THE HELIUM ION

THE elastic scattering of an electron by a helium ion differs from the elastic scattering of an electron by a hydrogen atom owing to the presence of the unscreened Coulomb field $\propto 1/r$ acting on the scattered electron. This Coulomb field modifies very significantly the scattering process and the form of the wave function, and its effect is not simply additive to that due to the hydrogen atom (the two effects are additive only on the Born approximation). By analogy with the scattering of an electron by a hydrogen atom we shall begin with the approximation on which the helium ion is regarded as a centre of force. We can then use the theory given at the end of § 2 and the problem is reduced to the determination of the phases $\mu_1$.

In [76] the phase $\mu_0$ is calculated by a variational method, and also (at two energies) by a numerical integration of the equation

$$\frac{d^2f}{dr^2}+\left(k^2+\frac{2}{r}-2w\right)f=0 \tag{23.1}$$

The formula for $w$ is

$$w=-\frac{1}{r}+\int\frac{|\psi|^2}{|r-r'|}dr'$$

where $\psi = 8^{\frac{1}{2}}\pi^{-\frac{1}{2}}\exp(-2r)$ is the wave function for the ground state of the He$^+$ ion, so that

$$w=-\left(2+\frac{1}{r}\right)e^{-4r} \tag{23.2}$$

In [76] the function $f$ is normalized so that it has the asymptotic form

$$f = F+\tan\mu G, \qquad r\rightarrow\infty \tag{23.3}$$

where $F$ is a regular Coulomb function having the asymptotic form

$$F\sim\sin\left(kr-\frac{\pi}{2}+\frac{1}{k}\ln 2kr+\eta\right) \tag{23.4}$$

and $G$ is a non-regular function with the asymptotic form

$$G\sim\cos\left(kr-\frac{\pi}{2}+\frac{1}{k}\ln 2kr+\eta\right) \tag{23.5}$$

According to (2.68) and (2.71) the scattering amplitude $q$ may be written as the sum

$$q = q_C + \frac{e^{2i\eta}}{2ik}(e^{2i\mu}-1) \tag{23.6}$$

where $q_C$ is the Coulomb scattering amplitude. As a measure of the departure of the actual scattering from the purely Coulomb scattering, the authors of [76] used the quantity

$$R = \left|\frac{q}{q_C}\right|^2 \tag{23.7}$$

From (23.6)

$$R = \left|1 + \frac{1}{q_C} e^{2i\eta} \frac{1}{2ik}(e^{2i\mu}-1)\right|^2 \tag{23.8}$$

When exchange is taken into account, (23.1) is replaced by

$$\frac{d^2f}{dr^2} + \left(k^2 + \frac{4}{r} - 2w\right)f = 2\int_0^\infty \mathscr{W}(r,r')f(r')\,dr' \tag{23.9}$$

In the present case

$$\mathscr{W}(r,r') = \pm 32 r\, e^{-2r} r'\, e^{-2r'}\left[-\frac{k^2}{2} + \frac{1}{2} + \gamma(r,r')\right] \tag{23.10}$$

Equation (23.9) was also solved numerically for two values of the energy. Moreover, the phase $\mu^\pm$ was found with the aid of a variational method. The trial function was taken in the form

$$f = F + (a + b\,e^{-2r})(1 - e^{-2r})G \tag{23.11}$$

The trial function for the electron plus ion system containing the interelectron distance $r_{12}$ was also employed. The quantities $R_+$ and $R_-$, calculated with allowance for exchange, were averaged using the formula

$$R = \tfrac{1}{4}R_+ + \tfrac{3}{4}R_- \tag{23.12}$$

The results of the variational calculation were found to be strongly dependent on the particular method employed, especially at low energies in the symmetric case. This suggests that the trial function was not very satisfactory. The numerical values of $\mu$ are given in Table 9, and a comparison of the results of the numerical integration and the variational calculation is given in Table 10. The function $R(\theta)$ at an energy of 48·84 eV is shown in Fig. 35.

A calculation of the excitation of $2s$ and $2p$ states of the helium ion with allowance for the $1s-2s-2p$ coupling is reported in [77] and [77a]. The calculation is quite analogous to that for the hydrogen atom. The partial wave equations are similar to the equations derived in Section 11, except that the functions $u_\mu$ and $v_\mu$ are the corresponding continuous-spectrum wave functions for the Coulomb field. The presence of the unscreened Coulomb field has an important effect on the behaviour of the amplitud

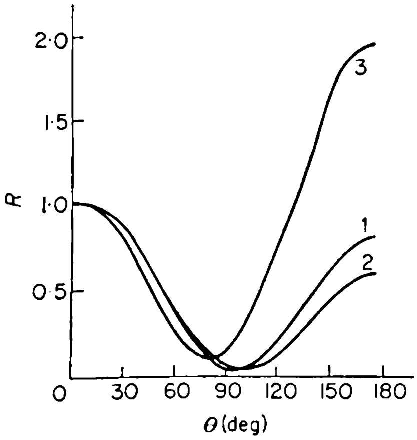

FIG. 35. A plot of the function $R(\theta)$ for $E = 48{\cdot}84$ eV: 1—without exchange and polarization, 2—with exchange, 3—with exchange and polarization

TABLE 9

| $E$ (eV) | $\mu$ with exchange | $\mu^-$ | $\mu^+$ | |
|---|---|---|---|---|
| | | | Kohn's method | Hulthén's method |
| 3·28 | 0·571 | 0·959 | −0·281 | 0·419 |
| 8·25 | 0·554 | 0·824 | 0·038 | 0·404 |
| 15·74 | 0·531 | 0·807 | 0·073 | 0·365 |
| 24·90 | 0·509 | 0·762 | 0·110 | 0·333 |
| 48·4 | 0·460 | 0·645 | 0·240 | 0·315 |
| 65·49 | 0·443 | 0·604 | 0·226 | 0·307 |

TABLE 10

| $E$ (eV) | $\mu$ without exchange | | $\mu^+$ | | | $\mu^-$ | |
|---|---|---|---|---|---|---|---|
| | Numerical calc. | Variational calc. | Numerical integration | Kohn's method | Hulthén's method | Numerical integration | Variational calc. |
| 48·4 | 0·468 | 0·460 | 0·288 | 0·240 | 0·315 | 0·648 | 0·645 |
| 65·49 | 0·443 | 0·443 | 0·283 | 0·226 | 0·307 | 0·604 | 0·604 |

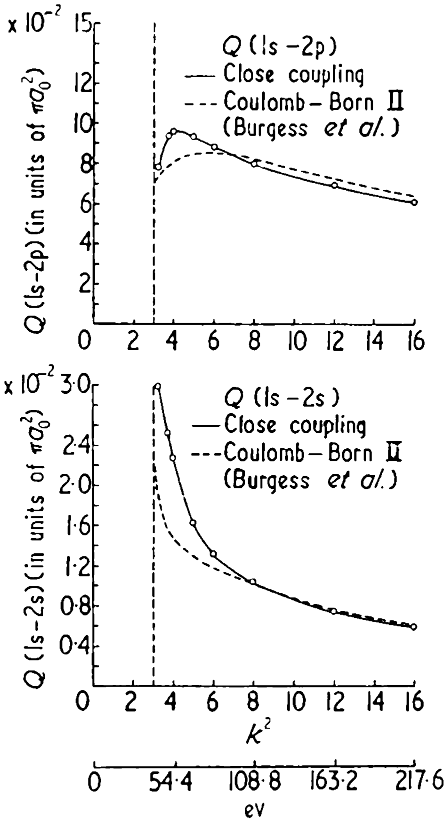

FIG. 35A. (Reproduced with permission from Burke *et al.* [77])

near the threshold. In particular, it is found that as the energy tends to the threshold value, the excitation amplitude increases without limit as $k^{-\frac{1}{2}}$. This is a consequence of the behaviour of the normalization factor $C_0$, given by (3.30), as $k \to \infty$. It is the reason why the excitation cross-section $\sigma = 4\pi(k_1/k_0)|q|^2$ remains finite when $k = 0$.

Figure 35A shows the excitation cross-section for the 2$s$ and 2$p$ levels of He$^+$ based on the data reported in [77].

## *Chapter 7*

# THE COLLISION OF AN ELECTRON WITH A HELIUM ATOM

## 24. THE WAVE FUNCTION FOR A THREE-ELECTRON SYSTEM

THE form of the wave function with a given spin and the required symmetry with respect to the spin and coordinate variables for a system of three or more electrons is not so apparent as in the case of a two-electron system.

There are a number of ways of constructing such wave functions in the form of a suitably symmetrized sum of products of coordinate functions and spin functions. The various methods of doing this are reviewed in [78] from the point of view of group theory.

Consider the wave function $\Phi(\boldsymbol{r}_1, \sigma_1, \ldots, \boldsymbol{r}_N, \sigma_N)$ of an $N$-electron system. It should be antisymmetric with respect to the interchange of any pair $(\boldsymbol{r}_i, \sigma_i)$ and $(\boldsymbol{r}_k, \sigma_k)$. We shall require that it should be the eigenfunction of the square of the spin angular momentum, so that

$$\hat{S}^2\Phi = s(s+1)\Phi \tag{24.1}$$

V. A. Fock [79] showed that an antisymmetric function satisfying (24.1) can be expressed in terms of the coordinate function $\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_k|\boldsymbol{r}_{k+1}, \ldots, \boldsymbol{r}_N)$ and the spin function $\chi(\sigma_1, \ldots, \sigma_k|\sigma_{k+1}, \ldots, \sigma_N)$. Henceforth we shall write $\Psi(1, \ldots, k|k+1, \ldots, N)$ and $\chi(1, \ldots, k|l+1, \ldots, N)$ instead of $\Psi(\boldsymbol{r}_1|\boldsymbol{r}_N)$ and $\chi(\sigma_1|\sigma_N)$, or simply $\Psi$, $\chi$, whenever this does not introduce an ambiguity. The vertical line separating $1, \ldots, k$ from $k+1, \ldots, N$ represents the division of the electrons into two swarms with opposite spin components. The number of electrons $k$ which make up the swarm $1, \ldots, k$ is related to the spin quantum number by

$$k = \frac{N}{2} - s \tag{24.2}$$

The functions $\Psi$ and $\chi$ have the following symmetry properties with respect to the exchange of the arguments:

1. The function $\Psi$ is antisymmetric with respect to the interchange of the arguments before or after the vertical line; this may be expressed in terms of the exchange operator $P_{i,j}$ in the form

$$(1+P_{i,j})\Psi = 0, \qquad i,j \leqslant k \qquad \text{or} \qquad i,j \geqslant k \tag{24.3}$$

2. $\Psi(1, \ldots, k|k+1, \ldots, N)$ exhibits cyclic symmetry, i.e.

$$\left(1 - \sum_{j=k+1}^{N} P_{k,j}\right)\Psi = 0 \tag{24.4}$$

3. The function $\chi$ is symmetric with respect to the interchange of the arguments before or after the vertical line, i.e.

$$(1-P_{i,j})\chi = 0, \qquad i,j \leqslant k \quad \text{or} \quad i,j \geqslant k \tag{24.5}$$

Consider the expression

$$\Phi = \sqrt{\frac{k!(N-k)!}{N!}} \sum_{\lambda_1,\dots,\lambda_k} (-1)^{\Lambda}\Psi(\lambda_1,\dots,\lambda_k|\lambda_{k+1},\dots,\lambda_N) \times \chi(\lambda_1,\dots,\lambda_k|\lambda_{k+1},\dots,\lambda_N) \tag{24.6}$$

where $\lambda_1, \dots, \lambda_N$ is a set of $N$ unequal numbers from among the sequence $1, \dots, N$, and $\Lambda$ is the parity of the permutation $\begin{pmatrix} 1 & 2 & \dots & N \\ \lambda_1 & \lambda_2 & \dots & \lambda_N \end{pmatrix}$. In view of (24.3)–(24.5), the function (24.6) is antisymmetric with respect to the interchange of $\boldsymbol{r}_i$, $\sigma_i$ and $\boldsymbol{r}_k$, $\sigma_k$. Next, using the well-known formula

$$\hat{S}^2 = N - \tfrac{1}{4}N^2 + \sum_{k<i} \varphi_{ik}^{(\sigma)} \tag{24.7}$$

which relates the operator $\hat{S}^2$ to the spin exchange operator $P_{ik}^{(\sigma)}$, and bearing in mind (24.2) and (24.4), it can be shown [79] that $\Psi$ is an eigenfunction of $\hat{S}^2$ with the eigenvalue $s(s+1)$. If $\chi$ is chosen to be of the form

$$\chi = \beta_1, \dots, \beta_k \alpha_{k+1}, \dots, \alpha_N \tag{24.8}$$

where

$$\alpha = \delta_{\sigma,1} \quad \text{and} \quad \beta = \delta_{\sigma,-1} \tag{24.9}$$

then $\Phi$ will also be an eigenfunction of $\hat{S}_z$ with the eigenvalue $s$. The coefficient $[(N-k)!k!/N!]^{\frac{1}{2}}$ in (24.6) ensures that when $\Psi$ and $\chi$ are normalized to unity, the function $\Phi$ is also normalized to unity.

In the case of the three-electron system there are two possible spin states, corresponding to $s = \frac{1}{2}$ and $s = \frac{3}{2}$. According to (24.2) the coordinate function corresponding to the first case is $\Psi(1|23)$, while the wave function corresponding to the second case is $\Psi(|123)$. The properties expressed by (24.3) and (24.4) can then be written in the following form:

$$(1+P_{\alpha,\beta})\Psi(|123) = 0, \qquad \alpha,\beta = 1,2,3 \tag{24.10}$$

$$(1+P_{23})\Psi(1|23) = 0 \tag{24.11}$$

$$(1-P_{12}-P_{13})\Psi(1|23) = 0 \tag{24.12}$$

The problem now arises as to how one can construct the two functions $\Psi(|123)$ and $\Psi(1|23)$ so that they will have the properties given by (24.10)–(24.12). It turns out that when an arbitrary function of three variables $\varphi(123)$ is symmetrized in accordance with Young's scheme, we obtain a function having the properties of $\Psi(1|23)$ or $\Psi(|123)$ depending on the form of the scheme.† This can be seen most easily in the case illustrated in Fig. 36(a) [57]. This scheme involves the action of the operator $(1-P_{12})(1-P_{13})(1-P_{23})$ on the function $\varphi(123)$. It is easy to see that the function

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† This was shown for an arbitrary number of electrons in [80].

$$\varphi_1 = (1-P_{12})(1-P_{13})(1-P_{23})\varphi(123) \tag{24.13}$$

satisfies (24.10) since, for example,

$$(1+P_{12})(1-P_{12}) = (1-P_{12}^2) = 0$$

It is also possible to carry out the symmetrization in accordance with the scheme illustrated in Fig. 36(b). This corresponds to the application of the operator $(1-P_{23})(1+P_{12})$. Consider the function

$$\varphi_2 = (1-P_{23})(1+P_{12})\varphi(123) \tag{24.14}$$

It satisfies the condition given by (24.11) since

$$(1+P_{23})(1-P_{23}) = 0$$

It also satisfies (24.12) since (as can be shown by direct calculation)

$$(1-P_{12}-P_{13})(1-P_{23})(1+P_{12})\varphi(123) = 0 \tag{24.15}$$

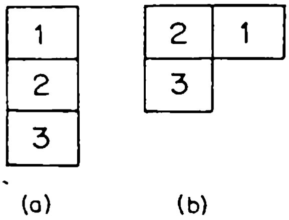

FIG. 36. Young's scheme: (a) for the function $\varphi_1 = \psi(|1\ 2\ 3)$; (b) for the function $\varphi_2 = \psi(1|2\ 3)$

It follows that the functions $\Psi(1|23)$ and $\Psi(|123)$ can be obtained from an arbitrary function of three variables by means of the Young symmetrization scheme of Figs. 36(a) and 36(b) respectively, namely, $\Psi(|123) = \varphi_1$ and $\Psi(1|23) = \varphi_2$.

The above analysis is concerned with the general case of a three-electron system. Since we shall be dealing with the collision of an electron with a helium atom, we shall consider three-electron functions $\Psi(1|23)$ and $\Psi(|123)$ of a special form, constructed by combining two-electron and one-electron functions. Since in the ground state the spin of the helium atom is zero, the only function which is of interest in practice is $\Psi(1|23)$. The function $\Psi(|123)$ can only be useful in the case of transitions between triplet states of the helium atom as a result of a collision with an electron, and we shall therefore confine our attention to the function $\Psi(1|23)$.

The function $\Psi(1|23)$ can include two forms of two-electron functions, namely, symmetric $\psi(1|2)$ and antisymmetric $\psi(|12)$. This is a consequence of the law of addition of angular momenta. The state of a three-electron system corresponding to spin $\frac{1}{2}$ may be formed by combining a one-electron state with both a singlet and a triplet state of a two-electron system. This can also be expressed in Young's terminology: the scheme shown in Fig. 36(b) may be constructed in two ways, as shown in Fig. 37. Accordingly, there are two expressions for $\Psi(1\,|\,23)$, namely,

$$\Psi_1(1|23) = c_1[\psi(1|2)F(3) - \psi(1|3)F(2)] \tag{24.16}$$

$$\Psi_2(1|23) = c_2[\psi(|12)F(3) - \psi(|13)F(2) + 2\psi(|32)F(1)] \tag{24.17}$$

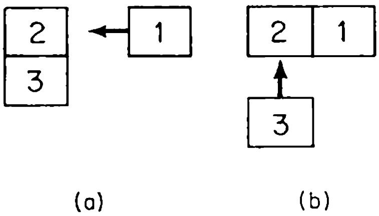

Fig. 37. Two ways of constructing Young's scheme for the function $\varphi(1|2\;3)$: (a) addition of a cell to the scheme for $\psi$ $(|2\;3)$; (b) addition of a cell to the scheme for $\psi(1|2)$

It can be easily verified that these expressions exhibit all the properties which the function $\Psi(1\,|\,23)$ should show. A general formula for the construction of $(n+1)$-electron functions from $n$-electron and 1-electron functions will be given in Chapter 8. The expressions given by (24.16) and (24.17) can be obtained from this formula as a special case. The coefficients $c_1$ and $c_2$ are the normalization coefficients. Suppose that $F$ refers to the continuous spectrum and is normalized as a plane wave, i.e.

$$\int F^*(k, r)F(k', r)\,dr = (2\pi)^3\delta(k-k') \tag{24.18}$$

Suppose further that $\psi(r_1\,|\,r_2)$ and $\psi(\,|\,r_1, r_2)$ refer to the discrete spectrum, and are normalized to unity:

$$\int |\psi(r_1|r_2)|^2\,dr_1\,dr_2 = 1, \qquad \int |\psi(|r_1, r_2)|^2\,dr_1\,dr_2 = 1 \tag{24.19}$$

If it is required that $\Psi(r_1\,|\,r_2, r_3)$ should also be normalized as a plane wave, i.e.

$$\int \Psi_k^*\Psi_{k'}\,dr_1\,dr_2\,dr_3 = (2\pi)^3\delta(k-k') \tag{24.20}$$

then we must set

$$c_1 = \frac{1}{\sqrt{2}}, \qquad c_2 = \frac{1}{\sqrt{6}} \tag{24.21}$$

The connection between these coefficients and the normalization of the spin functions will be established in § 25.

## 25. Equations for the Wave Function of the Scattered Electron

Starting from equations (24.16) and (24.17) we can write the coordinate wave function for the electron plus helium atom system in the form

$$\begin{aligned}\Psi(r_1|r_2,r_3) &= \frac{1}{\sqrt{2}}\sum_A [\psi_A(r_1|r_2)F_{A1}(r_3)-\psi_A(r_1|r_3)F_{A1}(r_2)]\\ &+\frac{1}{\sqrt{6}}\sum_A [\psi_A(|r_1,r_2)F_{A2}(r_3)-\psi_A(|r_1,r_3)F_{A2}(r_2)\\ &\qquad +2\psi_A(|r_3,r_2)F_{A2}(r_1)]\end{aligned} \tag{25.1}$$

where $\psi_A(r_1|r_2)$ and $\psi_A(|r_1,r_2)$ are the coordinate functions respectively of the singlet and triplet states of the helium atom. In the simplest approximation, they can be constructed from the one-electron functions:

$$\psi_A(1|2)=\psi(1)\varphi(2)+\psi(2)\varphi(1)$$

$$\psi_A(|12)=\psi(1)\varphi(2)-\varphi(2)\psi(1)$$

The functions $F_{A_a}(r)$ describe the state of the scattered electron. The subscript $A$ represents all the quantum numbers characterizing the state of the atom, and $a = 1, 2$ represents the two possible combinations of the spins of the atom and the incident electron.

The equations for $F_{A1}$ and $F_{A2}$ may be obtained from relationships analogous to (10.24):

$$\int \psi_A(r_1|r_2)(H-\mathscr{E})\Psi(r_1|r_2,r_3)\,dr_1\,dr_2=0 \tag{25.2}$$

$$\int \psi_A(|r_1,r_2)(H-\mathscr{E})\Psi(r_1|r_2,r_3)\,dr_1\,dr_2=0 \tag{25.3}$$

where $H$ is the energy operator for the electron plus helium atom system and is given by

$$H=-\tfrac{1}{2}\Delta_1-\tfrac{1}{2}\Delta_2-\tfrac{1}{2}\Delta_3+\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{23}}-\frac{2}{r_1}-\frac{2}{r_2}-\frac{2}{r_3},\quad r_{ik}\equiv|r_i-r_k| \tag{25.4}$$

The energy $\mathscr{E}$ of the system is made up of the energy of the atom prior to the collision and the energy of the incident electron.

Let us substitute equations (25.1) and (25.4) into (25.2) and (25.3). We shall take into account the symmetry properties and normalization of $\psi_A(r_1|r_2)$ and $\psi_A(|r_1,r_2)$, and will assume that the latter two functions satisfy the equations

$$\int \psi_A^*(r_1|r_2)\left(-\tfrac{1}{2}\Delta_1-\tfrac{1}{2}\Delta_2-\frac{2}{r_1}-\frac{2}{r_2}+\frac{1}{|r_1-r_2|}\right)\psi_{A'}(r_1|r_2)\,dr_1\,dr_2=0 \tag{25.5}$$

$$\int \psi_A^*(|r_1,r_2)\left(-\tfrac{1}{2}\Delta_1-\tfrac{1}{2}\Delta_2-\frac{2}{r_1}-\frac{2}{r_2}+\frac{1}{|r_1-r_2|}\right)\psi_{A'}(|r_1,r_2)\,dr_1\,dr_2=0,\quad A'\neq A \tag{25.6}$$

These equations are satisfied if $\psi_A$ and $\psi_{A'}$ are the exact atomic functions, but they may also be satisfied by approximate atomic functions.

Let

$$\mathscr{E} = \tfrac{1}{2}k_{Aa}^2 + E_{Aa} \tag{25.7}$$

where $E_{Aa}$ is the energy of the atom and $\frac{1}{2}k_{Aa}^2$ is the energy of the incident electron.† After some simple rearrangement, we have the following system of equations for $F_{Aa}$

$$\Delta F_{Aa}(r_3) + k_{Aa}^2 F_{Aa}(r_3) = 2\sum_{A'a'} \Big[V_{AA'a}(r_3)\delta_{a'a}F_{A'a}(r_3) + \int W_{AA'aa'}(r_1, r_3)F_{A'a'}(r_1)\,dr_1\Big] \tag{25.8}$$

where the potential energy matrix $V_{AA'a}$ is given by

$$V_{AA'a}(r_3) = -\frac{2}{r_3}\delta_{AA'} + 2\int \frac{\rho_{AA'a}(r_1)}{|r_3 - r_1|}\,dr_1 \tag{25.9}$$

with

$$\begin{aligned} \rho_{AA'1} &= \int \psi_A^*(r_1|r_2)\psi_{A'}(r_1|r_2)\,dr_2 \\ \rho_{AA'2} &= \int \psi_A^*(|r_1, r_2)\psi_{A'}(|r_1, r_2)\,dr_2 \end{aligned} \tag{25.10}$$

The exchange operators $W_{AA'aa'}$ are of the form

$$W_{AA'11}(r_1, r_3) = -\int \psi_A^*(r_1|r_2)(H - \mathscr{E})\psi_{A'}(r_2|r_3)\,dr_2 \tag{25.11}$$

$$W_{AA'12}(r_1, r_3) = -\sqrt{3}\int \psi_A^*(r_1|r_2)(H - \mathscr{E})\psi_{A'}(|r_3, r_2)\,dr_2 \tag{25.12}$$

$$W_{AA'21}(r_1, r_3) = -\sqrt{3}\int \psi_A^*(|r_1, r_2)(H - \mathscr{E})\psi_{A'}(r_3|r_2)\,dr_2 \tag{25.13}$$

$$W_{AA'22}(r_1, r_3) = -\int \psi_A^*(|r_1, r_2)(H - \mathscr{E})\psi_{A'}(|r_3, r_2)\,dr_2 \tag{25.14}$$

The expressions for the exchange operators can be transformed further. To begin with, consider the operator $-\frac{1}{2}\Delta_1$ in $H$. Since this operator is self-adjoint, we can replace $\psi_A(r_1\,|\,r_2)\Delta_1 F_{A1}(r_1)$ in equations (25.11)–(25.14) by $F_{A1}(r_1)\Delta_1\psi_A(r_1\,|\,r_2)$. A similar replacement may be carried out in the terms containing the function $\psi_A(r_1\,|\,r_2)$. Next, if $\psi_A(r_1\,|\,r_2)$ and $\psi_A(|\,r_1, r_2)$ are the exact wave functions for the helium atom, we can employ the conventional equations for them. As a result, the exchange operators assume the form

$$W_{AA'aa'}(r_1, r_3) = -\left[\left(\tfrac{1}{2}\Delta_1 + \frac{1}{r_{31}} - \frac{2}{r_1}\right)\rho_{AA'aa'}(r_1, r_3) + \int \frac{\rho_{AA'aa'}(r_1, r_2, r_3)\,dr_2}{r_{12}}\right] \tag{25.15}$$

---

† When $\psi_A$ are the approximate functions, the quantity $E_{Aa}$ is the mathematical expectation of the energy of the atom calculated from this function.

where

$$\rho_{AA'11}(r_1, r_3) = \int \psi_A^*(r_1|r_2)\psi_{A'}(r_2|r_3)\,dr_2 \tag{25.16}$$

$$\rho_{AA'22}(r_1, r_3) = \int \psi_A^*(|r_1, r_2)\psi_{A'}(|r_2, r_3)\,dr_2 \tag{25.17}$$

$$\rho_{AA'12}(r_1, r_3) = \sqrt{3}\int \psi_A^*(r_1|r_2)\psi_{A'}(|r_2, r_3)\,dr_2 \tag{25.18}$$

$$\rho_{AA'21}(r_1, r_3) = \sqrt{3}\int \psi_A^*(|r_1, r_2)\psi_{A'}(r_2|r_3)\,dr_2 \tag{25.19}$$

$$\rho_{AA'11}(r_1, r_2, r_3) = \psi_A^*(r_1|r_2)\psi_{A'}(r_2|r_3) \tag{25.20}$$

$$\rho_{AA'12}(r_1, r_2, r_3) = \sqrt{3}\,\psi_A^*(r_1|r_2)\psi_{A'}(|r_2, r_3) \tag{25.21}$$

$$\rho_{AA'21}(r_1, r_2, r_3) = \sqrt{3}\,\psi_A^*(|r_1, r_2)\psi_{A'}(r_2|r_3) \tag{25.22}$$

$$\rho_{AA'22}(r_1, r_2, r_3) = \psi_A^*(|r_1, r_2)\psi_{A'}(|r_2, r_3) \tag{25.23}$$

In practice the equations must be simplified. In addition to the errors which appear as a result of the simplification and which are also encountered in problems concerned with the hydrogen atom we have here one further source of difficulty, namely, the fact that the atomic wave functions are only approximate. This leads to errors in $V$ and $W$.

The equations (25.8) must be augmented by the asymptotic conditions. We shall assume that

$$F_{Aa}(r) \sim e^{ik_{Aa}\mathbf{v}.\mathbf{r}}\delta_{Aa,A_0a_0} + q_{Aa}\frac{e^{ik_{Aa}r}}{r}, \qquad r \to \infty \tag{25.24}$$

Let us now consider the asymptotic behaviour of the complete wave function for the system (including the spin variables). We return to (25.1) and consider any one of the terms representing two discrete states of the atom in the sum over $A$:

$$\begin{aligned}\Psi_A(r_1|r_2, r_3) = {} & \frac{1}{\sqrt{2}}[\psi_A(r_1|r_2)F_{A1}(r_3) - \psi_A(r_1|r_3)F_{A1}(r_2)] \\ & + \frac{1}{\sqrt{6}}[\psi_A(|r_1, r_2)F_{A2}(r_3) - \psi_A(|r_1, r_3)F_{A2}(r_2) \\ & \qquad + 2\psi_A(|r_3, r_2)F_{A2}(r_1)]\end{aligned} \tag{25.25}$$

In addition to this term, the complete wave function also includes $\Psi_A(r_3|r_1, r_2)$ and $\Psi_A(r_2|r_3, r_1)$. According to (24.6) we have

$$\begin{aligned}\Phi(r_1\sigma_1, r_2\sigma_2, r_3\sigma_3) = {} & \frac{1}{\sqrt{3}}[\Psi_A(r_1|r_2, r_3)\beta_1\alpha_2\alpha_3 \\ & + \Psi_A(r_3|r_1, r_2)\beta_3\alpha_1\alpha_2 + \Psi_A(r_2|r_3, r_1)\beta_2\alpha_1\alpha_3]\end{aligned} \tag{25.26}$$

As $r_1 \to \infty$, only those terms remain in which $r_1$ enters into $F_{Aa}$; the remaining terms all vanish, i.e.

$$\Psi_A(r_1|r_2,r_3) \sim \frac{2}{\sqrt{6}}\psi_A(|r_3,r_2)F_{A2}(r_1)$$

$$\Psi_A(r_3|r_1,r_2) \sim -\frac{1}{\sqrt{2}}\psi_A(r_3|r_2)F_{A1}(r_1)-\frac{1}{\sqrt{6}}\psi_A(|r_3,r_2)F_{A2}(r_1)$$

$$\Psi_A(r_2|r_3,r_1) \sim \frac{1}{\sqrt{2}}\psi_A(r_2|r_3)F_{A1}(r_1)+\frac{1}{\sqrt{6}}\psi_A(|r_2,r_3)F_{A2}(r_1)$$

If we collect these terms and substitute them into (25.26), we obtain (when $r_1 \to \infty$)

$$\sqrt{3}\,\Phi(r_1\sigma_1,r_2\sigma_2,r_3\sigma_3) \sim F_{A1}(r_1)\psi_A(r_2|r_3)\alpha_1\frac{\alpha_3\beta_2-\alpha_2\beta_3}{\sqrt{2}}$$
$$+F_{A2}(r_1)\psi_A(|r_3,r_2)\frac{2\beta_1\alpha_2\alpha_3-\beta_3\alpha_1\alpha_2-\beta_2\alpha_1\alpha_3}{\sqrt{6}} \tag{25.27}$$

The functions

$$\chi_1=\frac{1}{\sqrt{2}}\alpha_1(\beta_2\alpha_3-\beta_3\alpha_2) \tag{25.28}$$

and

$$\chi_2=\frac{1}{\sqrt{6}}[2\beta_1\alpha_2\alpha_3-\alpha_1(\alpha_3\beta_2+\alpha_2\beta_3)] \tag{25.29}$$

are the spin functions for the electron + helium atom system which are normalized to unity (normalization is ensured by choosing $c_1$ and $c_2$ in accordance with (24.21)). The function $\chi_1$ describes the state of the system in which the atom has zero spin, and the $z$-component of the spin of the incident electron along a special direction is $+\frac{1}{2}$. The function $\chi_2$ describes the superposition of the following two spin states:

(a) The triplet state of the atom with the spin $z$-component equal to 1 and the state of the incident electron with the spin $z$-component equal to $-\frac{1}{2}$.

(b) The triplet state of the atom with the $z$-component equal to 0 and the state of the incident electron with $z$-component equal to $+\frac{1}{2}$.

Therefore the wave function for the singlet state of the atom constructed in accordance with (24.6) is

$$\varphi_{A2}(r_2\sigma_2,r_3\sigma_3)=\psi_A(r_2|r_3)\frac{1}{\sqrt{2}}(\alpha_3\beta_2-\alpha_2\beta_3) \tag{25.30}$$

The expression

$$\varphi_{A2}(r_2\sigma_2,r_3\sigma_3)=\psi_A(|r_2,r_3)\alpha_2\alpha_3 \tag{25.31}$$

is the wave function for the triplet state of the atom, constructed in accordance with (24.6) with the spin $z$-component of the atom equal to 1. The expression

$$\varphi'_{A2}(r_2\sigma_2, r_3\sigma_3) = \psi_A(|r_3, r_2)\frac{\alpha_3\beta_2+\alpha_2\beta_3}{\sqrt{2}} \tag{25.32}$$

is also the function for the triplet state, but with zero spin $z$-component.

In view of (25.30)–(25.32) and (25.24), we can rewrite (25.27) in the form

$$\sqrt{3}\,\Phi\,(r_1\sigma_1, r_2\sigma_2, r_3\sigma_3) \underset{r_1\to\infty}{\sim} \varphi_{A1}q_{A1}\alpha_1\frac{e^{ik_{A1}r_1}}{r_1} + \varphi_{A2}q_{A2}\beta_1\sqrt{\frac{2}{3}}\frac{e^{ik_{A2}r_1}}{r_1} + \varphi'_{A2}q_{A2}\alpha_1\sqrt{\frac{1}{3}}\frac{e^{ik_{A2}r_1}}{r_1} \tag{25.33}$$

The current density along the $r_1$ axis in configuration space yields the cross-section for the excitation of the singlet state

$$d\sigma_1 = \frac{k_{A1}}{k_0}|q_{A1}|^2\,d\Omega \tag{25.34}$$

The excitation cross-section for the triplet state with spin $z$-component equal to 1 is

$$d\sigma_2^{(1)} = \frac{2}{3}\frac{k_{A2}}{k_0}|q_{A2}|^2\,d\Omega$$

whereas the excitation cross-section for the triplet state with zero spin $z$-component is

$$d\sigma_2^{(0)} = \frac{1}{3}\frac{k_{A2}}{k_0}|q_{A2}|^2\,d\Omega$$

On summing over all the possible spin components in the final state, we find that

$$d\sigma_2 = \frac{k_{A2}}{k_0}|q_{A2}|^2\,d\Omega \tag{25.35}$$

is the excitation cross-section for the triplet state with arbitrary spin $z$-component after collision.

## 26. ELASTIC SCATTERING OF AN ELECTRON BY A HELIUM ATOM

When polarization is neglected the elastic scattering of an electron by a helium atom is described by

$$\Delta F + (k^2 - 2V)F = 2\int WF\,dr' \tag{26.1}$$

where $V$ is defined by (25.9), (25.10) and $W$ by (25.11) or (25.15) through the ground state function $\psi(r_1|r_2)$ (the subscripts of $V$, $F$ and $W$ are omitted for simplicity).

The function $\psi(r_1|r_2)$ may be represented approximately as a product of the one-electron functions

$$\psi(r_1|r_2) = u(r_1)u(r_2) \tag{26.2}$$

We then have

$$V = -\frac{2}{r} + 2\int \frac{|u(r')|^2\,dr'}{|r-r'|} \tag{26.3}$$

The kernel of the exchange operator in (25.11) is

$$W(r',r) = u(r)\left[\tfrac{1}{2}\Delta_r + \tfrac{1}{2}\Delta_{r'} + \frac{2}{r} + \frac{2}{r'} - \frac{1}{|r-r'|} + \tfrac{1}{2}k_0^2 + E_0 + \int u(r'')\left(\tfrac{1}{2}\Delta'' + \frac{2}{r''} - \frac{1}{|r'-r''|} - \frac{1}{|r-r''|}\right)u(r'')\,dr''\right]u(r') \tag{26.4}$$

Using (25.15), we obtain

$$W(r',r) = u(r)\left[\tfrac{1}{2}\Delta_{r'} + \tfrac{1}{2}k_0^2 + \frac{2}{r'} - \frac{1}{|r-r'|} - \int \frac{u^2(r'')\,dr''}{|r''-r'|}\right]u(r') \tag{26.5}$$

The expressions given by (26.4) and (26.5) are, in general, different. However, they become identical in one important special case, namely, when $u(r)$ satisfies the equation for the self-consistent field

$$\Delta u + 2\left(\frac{2}{r} - \int \frac{u^2}{|r-r'|}\,dr'\right)u + 2\lambda u = 0 \tag{26.6}$$

and if instead of the exact energy $E$ of the helium atom, equation (26.4) contains the energy calculated by the self-consistent field method, i.e.

$$E_0 = 2\lambda - \int \frac{u^2(r)u^2(r')}{|r-r'|}\,dr\,dr' \tag{26.7}$$

Equation (26.6) may be used to reduce (26.5) to the even simpler form

$$W = u(r)u(r')\left(\tfrac{1}{2}k^2 + \lambda + \frac{1}{|r-r'|}\right) \tag{26.8}$$

which is analogous to the kernel of the exchange operator in the case of scattering of an electron by a hydrogen atom in the antisymmetric case [see equation (13.2)].

If the function $u(r)$ does not satisfy the equation for the self-consistent field, so that equation (26.4) cannot be reduced to (26.5), the problem arises as to which of them should be used in calculations. The variant represented by (26.4) was used in the calculations considered below [81, 82]. However, it may be argued that (26.5) is preferable. The point is that (26.4) and (26.5) differ considerably at small $r$: in (26.4) the function $W(r',r)$ includes the term $2/r$, whereas (26.5) does not include this term. When the replacement $(r_1, r_3) \to (r', r)$ is introduced into the exact expression (25.15), the function $W(r_1, r_3)$ does not contain $2/r$. Thus equation (26.5) is closer to the exact exchange operator than (26.4). The term $2/r$ in (26.4) appears only because the wave function is not exact.

Equations for the partial waves can be obtained by separating the angular variables in (26.1). Numerical integration of the equations for the $s$ and $p$ waves using the atomic functions for the self-consistent field was carried out as far back as 1933 [83]. The dependence of the phases $\delta_0$ and $\delta_1$ on the wave number which was obtained in that paper is illustrated in Fig. 38, together with the values of these phases without allowance for exchange. Morse and Allis used $\delta_0$ and $\delta_1$ to determine the angular distribution and the total scattering cross-section; they compared these with the experimental data existing at that time (see Figs. 39, 40). It is evident from these figures that, in general, the theoretical calculations reproduce quite satisfactorily the observed dependence of the cross-section on the energy

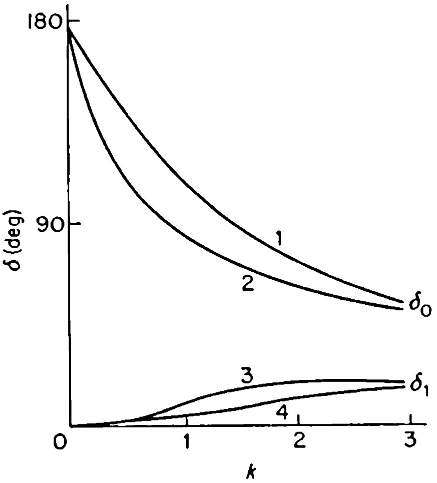

FIG. 38. Phases for an electron scattered by a helium atom: 1, 3—with exchange; 2, 4—without exchange

and the angular distribution, including the characteristic backward scattering maximum at 180° at low energies, which is similar to that observed in the case of the hydrogen atom (§ 17). Figure 39 can be used to determine the scattering length. It is found to be $a \approx 1{\cdot}5$ which corresponds to $\sigma = 4\pi a^2 \approx 28a_0^2$.

The scattering length was recently recalculated by numerical integration of the equation for $s$-waves of zero energy [82]. The one-electron atomic function $u(r)$ was chosen in the form

$$u(r) = N(e^{-Zr} + C\,e^{-2Zr}) \qquad (26.9)$$

where $N$ is the normalization factor and

$$C = 0{\cdot}6, \qquad Z = 1{\cdot}4558 \qquad (26.10)$$

This function is a good analytical approximation to the function for the self-consistent field: the calculation yields $a = 1{\cdot}442$, corresponding to $\sigma = 26{\cdot}1a_0^2$. The cross-section at zero energy obtained by extrapolation of the experimental data was found to be $\sigma = 22$.

Thus the numerical calculations in [82] lead to a result which exceeds the experimental value by only 18%. Part of this discrepancy is due to the fact that the polarization of the helium atom by the scattered electron was

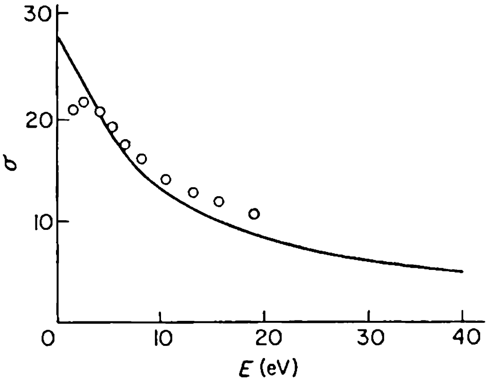

FIG. 39. Elastic scattering cross-section for an electron scattered by a helium atom (in units of $\pi a_0^2$): curve—theoretical, points—experimental

not included. Some of the error is due to the approximate nature of the wave function for the helium atom, including the fact that the approximate functions $\psi(r_1|r_2)$ given by (26.2) do not contain the distance $r_{12}$ between the electrons and therefore the correlation between the atomic electrons is ignored.

The variational method was used in connection with the scattering of an electron by a helium atom in [81]. The one-electron atomic function was taken in the simple form

$$u_0 = Ne^{-Zr} \tag{26.11}$$

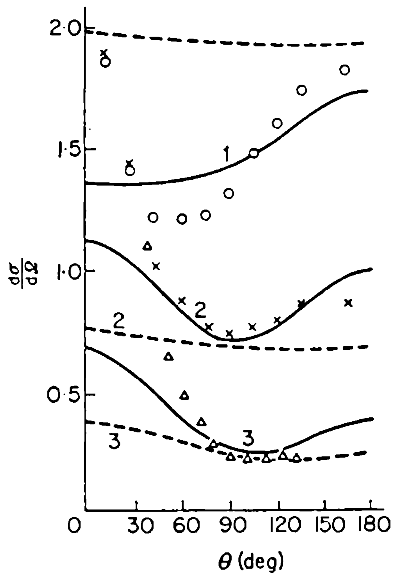

FIG. 40. Angular distribution of electrons scattered by a helium atom at electron energies of 6 eV (curve 1), 20 eV (curve 2) and 30 eV (curve 3). The broken curves represent theoretical calculations without exchange, the solid curves the theoretical values with exchange allowed for, and the points the experimental values

where

$$Z = \frac{27}{16}, \qquad N = \left(\frac{Z^3}{\pi}\right)^{\frac{1}{2}} \tag{26.12}$$

The exchange operator was determined with the aid of (26.4), using the approximate expression for the energy

$$E_0 = -2Z^2 \tag{26.13}$$

The trial function was chosen in the form

$$f = \sin kr + (a + b\, e^{-Zr})(1 - e^{-Zr}) \cos kr \tag{26.14}$$

The phase $\delta_0(k)$ obtained from these calculations is in good agreement with the results of numerical integration in spite of the fact that different one-electron atomic functions $u(r)$ were used in the two cases.

The scattering length determined by the variational method was $a = 1{\cdot}46$, quite close to the result obtained by numerical integration.

Finally, the phase $\delta_0$ was determined in [84] by an approximate solution of the integral equation for the $s$-wave. The resulting scattering length was found to be somewhat lower than that obtained by the variational method.

## 27. Excitation of the $2^1S$- and $2^3S$-states of the Helium Atom

The excitation of the $2^1S$- and $2^3S$-states of the helium atom was calculated in [85] by the distorted-wave approximation using the variational method; in [84] approximate expressions were obtained for the distorted waves with the aid of integral equations.

Here we shall confine our attention to the calculations described in [85]. On this approximation, the equations for the wave function of the scattered electron are

$$\Delta F_0 + (k_0^2 - 2V_{00})F_0 - 2\int W_{00} F_0\, d\mathbf{r}' = 0 \tag{27.1}$$

$$\Delta F_2 + (k_2^2 - 2V_{22})F_2 - 2\int W_{22} F_2\, d\mathbf{r}' = 2\left(V_{20}F_0 + \int W_{20} F_0\, d\mathbf{r}'\right) \tag{27.2}$$

$$\Delta F_1 + (k_1^2 - 2V_{11})F_1 - 2\int W_{11} F_1\, d\mathbf{r}' = 2\int W_{10} F_0\, d\mathbf{r}' \tag{27.3}$$

with the asymptotic behaviour

$$F_0 = e^{ik_0\mathbf{v}.\mathbf{r}} + q_0 \frac{e^{ik_0 r}}{r}, \qquad F_{1,2} = q_{1,2} \frac{e^{ik_{1,2} r}}{r} \tag{27.4}$$

The function $F_0$ describes the scattering of an electron when the target atom is in the ground state; $F_1$ and $F_2$ describe the excitation of the $2^3S$- and $2^1S$-states respectively. Following the distorted-wave method, we neglect $W_{21}F_1$ and $W_{12}F_2$, which connect the excitation of the triplet and singlet states, and the effect of the functions $F_2$ and $F_1$ on $F_0$. As can be seen from (27.3), excitation of the triplet state is only possible as a result of the exchange interaction $W_{10}$. The quantities $V_{\alpha\beta}$ and $W_{\alpha\beta}$ are determined from (25.9) and (25.11). The wave function for the ground state is taken in the form

$$\psi_0(r_1|r_2) = u_0(r_1)u_0(r_2) \tag{27.5}$$

where $u_0$ is given by (26.11). The wave function for the triplet $2^3S$-state is taken in the form

$$\psi_1(|r_1, r_2) = N_1[u_1(r_1)u_2(r_2) - u_2(r_1)u_1(r_2)] \tag{27.6}$$

with $u_1$ and $u_2$ given by [86]

$$\begin{aligned} u_1(r) &= e^{-\alpha r} \\ u_2(r) &= r\,e^{-\beta r} - c\,e^{-\gamma r} \end{aligned} \tag{27.7}$$

where

$$\alpha = 2, \qquad \beta = 0{\cdot}61, \qquad \gamma = 1{\cdot}57$$

and

$$c = \frac{3(\alpha+\gamma)^3}{(\beta+\alpha)^4}$$

The coefficient $c$ is chosen so that the function $u_1(r)$ is orthogonal to $u_2(r)$, and the parameters $\beta$, $\gamma$ determined from the condition for minimum energy. The function for the singlet $2^1S$-state is taken as

$$\psi_2(r_1|r_2) = N[u_1(r_1)u_2(r_2) + u_2(r_1)u_1(r_2)] \tag{27.8}$$

where $u_1(r)$ and $u_2(r)$ are in the same form as for the $2^3S$-state [equation (27.7)] in order to simplify the calculations. The parameters of the one-electron functions $u_1$ and $u_2$ are different for the triplet and singlet states when determined from the minimum energy condition.

The function $\psi_2(r_1|r_2)$ given by (27.8) is not orthogonal to $\psi_0(r_1|r_2)$. As a result $V_{20}$ includes terms which fall off as $r^{-1}$ when $r \to \infty$. In reality, $V_{20}$ should fall off exponentially when $r \to \infty$. For this reason, terms which behave as $r^{-1}$ when $r \to \infty$ are rejected in $V_{20}$, and this removes the most undesirable consequence of the fact that $\psi_0(r_1|r_2)$ and $\psi_2(r_1|r_2)$ are not orthogonal. There remains the error in the numerical value of the terms having the correct asymptotic behaviour, which is due to non-orthogonality. This error was not estimated in [85]. Only the $s$-waves were taken into account in the expansion of $F_\alpha$ into the partial waves. Therefore the problem reduces to the determination of the three functions

$$\begin{aligned} {}_0(r) &= rF_0(r) \\ f_{1,2}(r) &= r\mathscr{F}_{1,2}(r) \end{aligned} \tag{27.9}$$

where $\mathscr{F}_1(r)$ and $\mathscr{F}_2(r)$ are the solutions of (27.2) and (27.3) without the right-hand side terms; $f_1$ and $f_2$ have the asymptotic behaviour

$$f_\alpha \sim \frac{1}{k_\alpha} e^{i\eta_\alpha} \sin(k_\alpha r + \eta_\alpha) \tag{27.10}$$

The amplitudes $q_1$ and $q_2$ are expressed in terms of $f_0, f_1$ ,and $f_2$ by formulae analogous to (18.27).

The latter three functions are determined by a variational technique. The trial function $f_0$ is chosen to be analogous to (26.14). When the asymptotic behaviour given by (27.10) is taken into account, the trial function becomes

$$f_0 = \frac{e^{i\eta_0}}{k_0}(1+a^2)^{-\frac{1}{2}}[\sin k_0 r + (a+b\,e^{-Zr})(1-e^{-Zr})\cos k_0 r] \qquad (27.11)$$

where $Z = 27/16$.

The trial functions for $f_1$ and $f_2$ are taken to be

$$f_1 = \frac{e^{i\eta_1}}{k_1}(1+\lambda_1^2)^{-\frac{1}{2}}[(1+C\,e^{-r})\sin k_1 r + \lambda_1(1-e^{-r})\cos k_1 r] \qquad (27.12)$$

and similarly for $f_2$. Calculations show that (27.12) is a very poor approximation for $f_2$ at low energies near $k_2 = 0$, and therefore $\eta_2$ and $q_2$ are calculated for $k_2 \geqslant 0{\cdot}3$. The corresponding effective cross-section is shown in Fig. 41. For $\eta_1$ and $q_1$ the calculation is carried out with $k_1 > 0{\cdot}1$, and a determination is made of the scattering length for the $2^3S$-state of the atom (although the numerical result is not given in [85]).

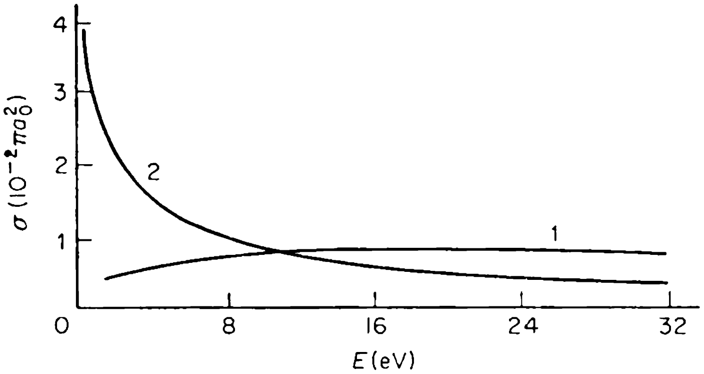

FIG. 41. Partial cross-sections for the excitation of the $2^1S$ (curve 1) and $2^3S$ (curve 2) states of helium at $l = 0$. The energy is measured from the threshold

In order to illustrate the importance of exchange, the parameters $\eta_1$ and $q_1$ have been calculated without introducing this effect. Figure 42 shows the dependence of $\eta_2$, $\eta_1$ and $\eta_{12}$ on $k$ without exchange. The broken curve shows the part determined on the basis of the estimated scattering length, i.e. the slope of the $\eta(k)$ curve for $k = 0$. As can be seen from the figure, even with relatively small changes corresponding to $k \gtrsim 0{\cdot}5$, the order of magnitude of the phase and its dependence on $k$ is very nearly the same with and without exchange. However, near the threshold ($k \sim 0{\cdot}1$–$0{\cdot}2$), the inclusion of exchange has a radical effect on the variation of the phases: the scattering length in the $2^3S$-state increases very rapidly as a result of exchange. The phase $\eta_1$ approaches $3\pi/2$ when $k = 0{\cdot}05$, i.e. very near the threshold. In other words, scattering by a helium atom in the $2^3S$-state is very close to resonance scattering. This is associated with the existence of a negative metastable He$^-$ state which lies about 0·1 eV above the $2^3S$-state of He.

The calculated excitation cross-section in the $2^3S$-state near the threshold is shown in Fig. 43, which also gives the experimental values [87]. As can be seen, the calculations show a much sharper peak near the threshold than is observed in experiment. This is not surprising when it is recalled that

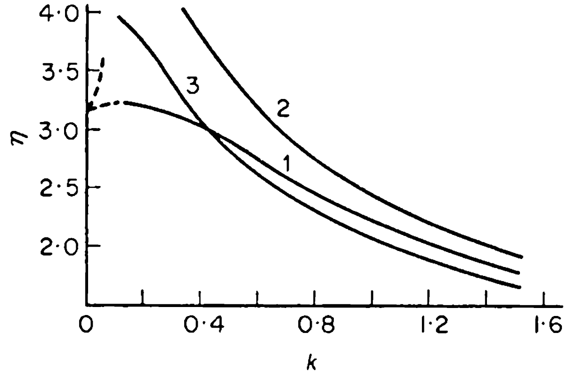

FIG. 42. The effect of exchange on the phases of trial functions: 1—phase $\eta_{1,2}$ with exchange, 2—$\eta_2$ and 3—$\eta_1$

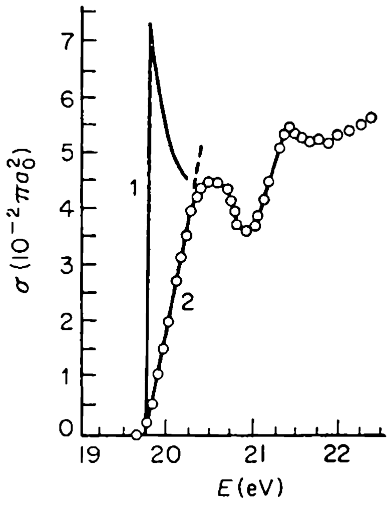

FIG. 43. The variation of the cross-section for the excitation of the $2^3S$-state of helium near the threshold: 1—calculated [75], 2—experimental [77]

scattering by a helium atom in the $2^3S$-state is very near to resonance scattering. Under such conditions, the phase $\eta_1$ and therefore the calculated cross-section for the $2^3S$-state, are very sensitive to small changes in the form of the wave function inside the atom, so that the variational method using simple trial functions is unsatisfactory. No exact numerical calculations have as yet been carried out.

A possible interpretation of the behaviour of the $2^3S$-state excitation cross-section near the threshold is given in [88], where it is suggested that inelastic electron scattering giving rise to excitation of the $2^3S$-state is analogous to nuclear reactions which proceed through the formation of a compound system (in the present case $He^-$ in the $2S_{\frac{1}{2}}$ state). If this is so, the effective cross-section for $s$-scattering near the threshold should be described by the Breit-Wigner formula

$$\sigma = \frac{\pi}{k_0^2} \frac{\Gamma_0 \Gamma_1}{(E-E_c)^2 + \frac{1}{4}(\Gamma_0+\Gamma_1)^2} \tag{27.13}$$

where $E_c$ is the energy of the compound system, $\Gamma_0$ is the width for the decay of the ion into an atom in the $^1S$-state and an electron, and $\Gamma_1$ is the width for the decay of the atom into an atom in the $2^3S$-state and an electron. The widths $\Gamma_0$ and $\Gamma_1$ may be written in the form

$$\Gamma_0 = 2k_0\gamma_0^2, \qquad \Gamma_1 = 2k_1\gamma_1^2 \tag{27.14}$$

$\Gamma_0$ and $\Gamma_1$ are the so-called reduced widths and are independent of energy.

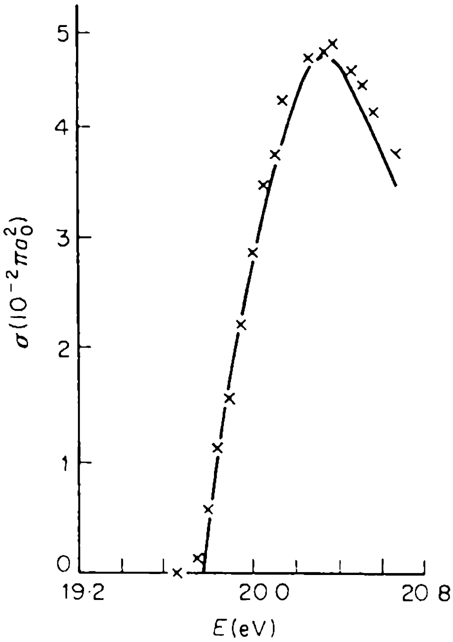

FIG. 44. Cross-section for the excitation of the $2^3S$-state of helium on the compound system model: curve—Breit-Wigner formula with the parameters given by (27.15), points—experimental values [77]. Excitation threshold $E_{th} = 19{\cdot}79$ eV

Figure 44 shows a plot of $\sigma(E)$ as given by (27.13), with the following empirical parameters

$$\begin{aligned} E_c &= 20{\cdot}19 \text{ eV} \\ \gamma_0^2 &= 2{\cdot}2 . 10^{-9} \text{ eV.cm} \\ \gamma_1^2 &= 2{\cdot}5 . 10^{-10} \text{ eV.cm} \end{aligned} \tag{27.15}$$

These values of the parameters are not the only ones to give adequate agreement with experiment. Another selection of the parameters is also discussed in [88].

For comparison, Fig. 44 also shows the experimental points, and as can be seen the agreement is quite good. The magnitude of $\gamma_{0,1}$ corresponds to a width $\Gamma \sim 1$ eV or a lifetime $\sim 10^{-15}$ sec, which is of the same order as the half-life for the auto-ionization of He in the $2s^2\ {}^1S_0$ state (about $2{\cdot}5 \times 10^{-15}$ sec). The experimental $\sigma(E)$ curve exhibits one further feature.

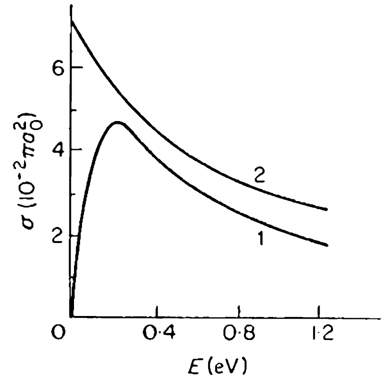

FIG. 45. Cross-sections for the excitation of the $2^3S$-state of helium: 1—experimental, 2—calculated for $l = 0$ and 1. $E$ is the energy measured from the threshold

It is found that near the threshold the values of $\sigma$ lie very nearly on a straight line and therefore in this region $\sigma$ may be regarded as a linear function of the energy measured from the threshold:

$$\sigma \sim (E - E_1)$$

However, it follows from the general expression $\sigma = (k_1/k_0) \int |q|^2 d\Omega$ that if $q$ remains constant for $k_1 = 0$, and this is certainly the case for neutral atoms, then $\sigma$ should be proportional to $k_1$, i.e.

$$\sigma \sim \sqrt{E - E_1}$$

It appears that the region near threshold where $q$ is approximately independent of energy and $\sigma \sim \sqrt{E - E_1}$ is very narrow and is not detected owing to the low resolving power of the instruments.

Direct comparison of the calculations of the partial cross-section for $l = 0$ with the experimental data at energies of a few eV above the threshold has no meaning because the partial wave with $l = 1$ introduces a considerable contribution at such energies. The contribution due to the $p$-wave was estimated in [85] with $V_{\alpha z}$ and $W_{\alpha z}$ neglected. The results are given in Fig. 45 together with experimental data.

## 28. THE $2^1S - 2^3S$ TRANSITION DURING A COLLISION WITH AN ELECTRON

The transition from the metastable $2^1S$-state to the lower $2^3S$-state in which the excess energy is given to the incident electron was discussed in

[89], in which the system of equations for the $s$-waves was numerically integrated on the strong coupling approximation. The equations were

$$\frac{d^2f_2}{dr^2} + (k_2^2 - 2\mathscr{V}_{22})f_2 - 2\int_0^\infty \mathscr{W}_{22} f_2\,dr' = 2\int_0^\infty \mathscr{W}_{21} f_1\,dr' \tag{28.1}$$

$$\frac{d^2f_1}{dr^2} + (k_1^2 - 2\mathscr{V}_{11})f_1 - 2\int_0^\infty \mathscr{W}_{11} f_1\,dr' = 2\int_0^\infty \mathscr{W}_{12} f_2\,dr' \tag{28.2}$$

with the asymptotic behaviour

$$f_2 \sim \frac{1}{k_2}\sin k_2 r + q_2 e^{ik_2 r}, \qquad f_1 \sim q_1 e^{ik_1 r} \tag{28.3}$$

where $f_2$ describes the incident electron with energy $\frac{1}{2}k_2^2$ and $f_1$ describes the electron after collision, with energy $\frac{1}{2}k_1^2 = \frac{1}{2}k_2^2 + \Delta E$. The partial cross-section for the process is

$$\sigma = 4\pi |q_1|^2 \frac{k_1}{k_2} \tag{28.4}$$

$\mathscr{V}_{\alpha\alpha}$ and $\mathscr{W}_{\alpha\beta}$ were calculated from the general formulae (25.9) and (25.11) using the analytical expression (27.7) for the atomic functions. Table 11 gives the results of the calculations, with the cross-sections $\sigma$ in units of $a_0^2$.

TABLE 11

| $k_1$ | $E$ (eV) | $\sigma$ |
|---|---|---|
| 0·044 | 0·026 | 180 |
| 0·050 | 0·034 | 141 |
| 0·060 | 0·048 | 113 |
| 0·100 | 0·134 | 64·7 |
| 0·300 | 1·210 | 14·6 |

The calculated cross-section at 0·026 eV is smaller than that observed by a factor of about six. This discrepancy may be due in part to the fact that the functions for the $2^1S$- and $1^1S$-states are not orthogonal. However, this would hardly lead to an error of this magnitude. Another possible explanation of the discrepancy is the formation of the metastable He$^-$ ion. However, no quantitative estimates of these effects are available.

## 29. EXCITATION OF SINGLET $n^1P$-STATES ($n$ = 2, 3, 4)

Excitation of the singlet $P$-states was analysed in [90] on the strong-coupling approximation, but without allowance for exchange effects.

In order to elucidate the relative importance of the various partial waves, a calculation was made of the cross-sections corresponding to total angular momenta $L = 0, 1, 2$ and 3. In the group of indices $\nu' = (n', l_1', l_2')$ referring to the initial state, $l_1' = 0$ for all the transitions under consideration while $l_2' = L$. In the group of indices $\nu = (n, l_1, l_2)$ referring to the final state, $l_1 = 1$, while $l_2$ can assume the values $|L-1| \leqslant l_2 \leqslant L+1$. When in accordance with the laws of composition of angular momenta there were more than two equations, they were split into independent pairs. Tables 12–14 give the calculated values of the effective excitation cross-sections for the levels $1^1S-3^1P$ ($E_{\text{th}} = 23{\cdot}308$ eV), $1^1S+2^1P$ ($E_{\text{th}} = 21{\cdot}211$ eV), and $1^1S = 4^1P$ ($E_{\text{th}} = 23{\cdot}734$ eV) in units of $\pi a_0^2/100$. As can be seen from these

TABLE 12

| $k_1$ | $E$ (eV) | $\sigma_{10}$ | $\sigma_{01}$ | $\sigma_{21}$ | $\sigma_{12}$ | $\sigma_{32}$ | $\sigma_{23}$ | $\sigma$ |
|---|---|---|---|---|---|---|---|---|
| 0·05 | 23·342 | 0·446 | 0·0$^3$20† | 0·172 | 0·0$^5$15 | 0·0$^4$46 | — | 0·649 |
| 0·10 | 23·444 | 0·245 | 0·0$^2$43 | 1·52 | 0·0$^5$35 | 0·0$^2$56 | 0·0$^5$37 | 1·808 |
| 0·20 | 23·852 | 0·166 | 0·210 | 3·52 | 0·0$^2$12 | 0·606 | 0·0$^4$12 | 4·503 |
| 0·40 | 25·484 | 0·132 | 0·430 | 2·72 | 0·0$^2$26 | 0·745 | 0·0$^2$12 | 4·031 |
| 0·60 | 27·204 | 0·102 | 0·366 | 2·12 | 0·0$^2$32 | 1·135 | 0·0$^2$47 | 3·731 |
| 0·80 | 32·012 | 0·074 | 0·298 | 1·52 | 0·0$^2$28 | 1·286 | 0·0$^2$978 | 3·191 |
| 1·0 | 36·908 | 0·0503 | 0·233 | 1·02 | 0·0$^2$17 | 1·220 | 0·0139 | 2·539 |

TABLE 13

| $k_1$ | $E$ (eV) | $\sigma_{10}$ | $\sigma_{01}$ | $\sigma_{21}$ | $\sigma_{12}$ |
|---|---|---|---|---|---|
| 0·05 | 21·245 | 1·13 | 0·0$^3$43 | 0·036 | — |
| 0·10 | 21·347 | 0·976 | 0·0$^2$13 | 0·291 | 0·0$^6$24 |
| 0·20 | 21·755 | 0·601 | 0·024 | 3·72 | 0·0$^5$68 |
| 0·60 | 25·107 | 0·274 | 1·28 | 9·16 | 0·0$^3$43 |
| 1·00 | 34·811 | 0·128 | 0·810 | 4·44 | 0·0$^4$20 |

TABLE 14

| $k_1$ | $E$ (eV) | $\sigma_{10}$ | $\sigma_{01}$ | $\sigma_{21}$ | $\sigma_{12}$ |
|---|---|---|---|---|---|
| 0·05 | 23·768 | 0·139 | 0·0$^3$25 | 0·250 | 0·0$^5$61 |
| 0·10 | 23·870 | 0·092 | 0·011 | 1·075 | 0·0$^3$10 |
| 0·20 | 24·278 | 0·075 | 0·541 | 1·210 | 0·0$^2$23 |
| 0·60 | 27·630 | 0·050 | 0·172 | 0·820 | 0·0$^2$27 |
| 1·00 | 37·334 | 0·026 | — | 0·406 | 0·0$^2$17 |

---

† Superscripts indicate number of zeros after the decimal point, for example 0·0$^3$43 = 0·00043.

tables, at the energy of only 1 eV above the threshold, the main contribution to the excitation cross-section is due to the partial cross-section $\sigma_{21}$. In some regions the latter is much greater than all the remaining cross-sections. The origin of this effect was discussed earlier in § 18.

TABLE 15

| $k_1$ | $E$ (eV) | $\sigma_{01}$ |  | $\sigma_{10}$ |  |
|---|---|---|---|---|---|
|  |  | s.-c. | d.-w. | s.-c. | d.-w. |
| 0·1 | 23·444 | $0{\cdot}0^{2}43$ | 0·044 | 0·245 | 0·233 |
| 0·6 | 27·204 | 0·366 | 0·346 | 0·102 | 0·096 |
| 1·0 | 36·908 | 0·233 | 0·186 | 0·050 | 0·040 |

The relative importance of strong coupling may be estimated from Table 15 which gives the cross-sections for the excitation of the $3^1P$-level (in units of $\pi a_0^2/100$) calculated by the distorted-wave (d.-w.) and the strong-coupling (s.-c.) approximations.

## *Chapter 8*

# GENERAL EQUATIONS DESCRIBING THE COLLISION OF AN ELECTRON WITH AN ARBITRARY ATOM OR ION

## 30. THE WAVE FUNCTION FOR THE ATOM + ELECTRON SYSTEM

CONSIDER an $(n+1)$-electron system consisting of an $n$-electron atom (ion) and an incident electron. According to § 24, the coordinate part of the wave function $\Psi(r_1, \ldots, r_k | r_{k+1}, \ldots, r_{n+1})$ is antisymmetric, i.e.

$$(1+P_{i,j})\Psi = 0 \tag{30.1}$$

if $i, j \leqslant k$ or $i, j > k$; it is also cyclically symmetric, i.e.

$$\left(1 - \sum_{i=k+1}^{n+1} P_{k,i}\right)\Psi = 0 \tag{30.2}$$

The number of terms on the left of the vertical line is related to the spin $s$ (which is assumed to be fixed):

$$k = \frac{n+1}{2} - s \tag{30.3}$$

By analogy with the treatment of the helium atom, we shall construct the function

$$\Psi(r_1, \ldots, r_k | r_{k+1}, \ldots, r_{n+1})$$

from the products of $n$-electron atomic functions $\psi$ and one-electron functions $F$, so that (30.1) and (30.2) are satisfied.

For a given square of the spin angular momentum of the $(n+1)$-electron system, there are two possible spin states of the sub-system of $n$-electrons, namely

$$s_1 = s - \tfrac{1}{2}, \qquad s_2 = s + \tfrac{1}{2}$$

The corresponding functions are

$$\psi_1(1, \ldots, j_1 | j_1 + 1, \ldots, n) \quad \text{and} \quad \psi_2(1, \ldots, j_2 | j_2 + 1, \ldots, n)$$

According to equation (30.3),

$$j_1 = \tfrac{1}{2}n - (s - \tfrac{1}{2}) = k, \qquad j_2 = \tfrac{1}{2}n - (s + \tfrac{1}{2}) = k - 1 \tag{30.4}$$

We shall therefore consider the products of the $n$-electron function $\psi$ and one-electron functions $F$ of the form

$$\psi_1(1, \ldots, k | k+1, \ldots, n) F_1(n+1)$$

and

$$\psi_2(1, \ldots, k-1 | k, \ldots, n) F_2(n+1)$$

Consider the sums

$$\Psi_1 = \sum_{i=k+1}^{n+1} a_i P_{i,n+1} \psi_1(1, \ldots, k|k+1, \ldots, n) F_1(n+1) \tag{30.5}$$

and

$$\Psi_2 = \sum_{t=1}^{k} \sum_{i=k}^{n+1} b_{t,i} P_{t,k} P_{i,n+1} \psi_2(1, \ldots, k-1|k, \ldots, n) F_2(n+1) \tag{30.6}$$

with the coefficients $a_i$ and $b_{t,\,i}$ chosen so that (30.1) and (30.2) are satisfied. It is understood that application of the exchange operator results in the following transformations

$$P_{ab} f(1, 2, \ldots, a, \ldots, b, \ldots, n) = f(1, 2, \ldots, b, \ldots, a, \ldots, n)$$

and

$$P_{ab} f(1, \ldots, a, \ldots, b, \ldots, n) g(1, \ldots, a, \ldots, b, \ldots, n)$$
$$= f(1, \ldots, b, \ldots, a, \ldots, n) g(1, \ldots, b, \ldots, a, \ldots, n)$$

i.e. the $a$-th and $b$-th arguments can be exchanged independently of their position within the brackets.

We note that all the steps necessary to obtain $a_i$ and $b_{t,\,i}$ may be performed in compact form by using the commutation relations

$$P_{ab} P_{bc} = P_{ac} P_{ab} = P_{bc} P_{ac} \tag{30.7}$$

These relations can easily be verified. For example,

$$P_{ab} P_{bc} f(abc) = P_{ab} f(acb) = f(bca)$$
$$P_{ac} P_{ab} f(abc) = P_{ac} f(bac) = f(bca)$$

The coefficients $a_i$ and $b_{i,\,t}$ are defined unambiguously to within a common factor which is unimportant and can be included in the normalization. We shall not go into details but will merely write down the final result and then verify (30.1) and (30.2) [91]. The expressions for $\Psi_1$ and $\Psi_2$ are of the form

$$\Psi_1 = c_1 \left(1 - \sum_{i=k+1}^{n} P_{i,n+1}\right) \psi_1(1, \ldots, k|k+1, \ldots, n) F_1(n+1) \tag{30.8}$$

$$\Psi_2 = c_2 \left(1 - \sum_{t=1}^{k-1} P_{t,k}\right) \left[1 - \sum_{i=k+1}^{n} P_{i,n+1} + (n-2k+2) P_{k,n+1}\right]$$
$$\times \psi_2(1, \ldots, k-1|k, \ldots, n) F_2(n+1) \tag{30.9}$$

The coefficients $c_1$ and $c_2$ can be defined from the normalization conditions. Suppose that $\psi_1$ and $\psi_2$ belong to the discrete spectrum while $F_1$ and $F_2$ belong to the continuous spectrum, and that $\psi_{1,2}$ are normalized to unity, but that $F_1$ and $F_2$ are normalized as a plane wave to $(2\pi)^3 \delta(k+k')$. If we require that $\Psi_1$ and $\Psi_2$ should also be normalized to $(2\pi)^2 \delta(k+k')$, then

$$\begin{aligned} c_1 &= (n-k+1)^{-\frac{1}{2}} \\ c_2 &= k^{-\frac{1}{2}} [(n-2k+2)^2 + (n-k+1)]^{-\frac{1}{2}} \end{aligned} \tag{30.10}$$

We shall now show that $\Psi_1$ satisfies (30.1) and (30.2) (the normalization factors will be omitted from the proof).

1. The anti-symmetry condition is clearly satisfied up to the vertical line, since the arguments of $\Psi_1$ and $\psi_1$ up to the line are identical.

2. In order to establish the anti-symmetry condition after the vertical line let us apply the operator $(1+P_{i,j})$ and use equation (30.7). The result is

$$(1+P_{i,j})\Psi_1 = \begin{cases} \left(1-\sum\limits_{l=k+1}^{n} P_{l,n+1}\right)(1+P_{i,j})\psi_1 F_1, & i,j \neq n+1 \\ -\sum\limits_{l\neq i} P_{l,n+1}(1+P_{i,l})\psi_1 F_1, & j = n+1 \end{cases}$$

which is zero because

$$(1+P_{i,l})\psi_1 = 0$$

3. The cyclic symmetry may be established as follows. From (30.7) it can be shown that

$$\left(1-\sum_{j=k+1}^{n+1} P_{k,j}\right)\left(1-\sum_{i=k+1}^{n} P_{i,n+1}\right) = \left(1-\sum_{j=k}^{n} P_{k,j+1}\right)\left(1-\sum_{j=k+1}^{n} P_{k,j}\right)$$

Since

$$\left(1-\sum_{j=k+1}^{n} P_{k,j}\right)\psi_1 = 0$$

it follows that

$$\left(1-\sum_{j=k+1}^{n+1} P_{k,j}\right)\Psi_1 = 0$$

The proof for $\Psi_2$ is quite similar.

1. The anti-symmetry condition up to the vertical line can be proved by operating with $(1+P_{i,j})$ on $\Psi_2$:

$$(1+P_{i,j})\Psi_2 = \begin{cases} \left(1-\sum\limits_{t=1}^{k-1} P_{t,k}\right)\left[1-\sum\limits_{j=k+1}^{n} P_{j,n+1}+(n-2k+2)P_{k,n+1}\right] \\ \qquad\qquad \times(1+P_{i,j})\psi_2 F_2, & i,j \neq n+1 \\ \left(1-\sum\limits_{t=1}^{k-1} P_{t,k}\right)\left[(n-2k+2)P_{k,n+1}(1+P_{i,k})\right. \\ \qquad\qquad \left. -\sum\limits_{t\neq l} P_{l,n+1}(1+P_{i,l})\right]\psi_2 F_2, & j = n+1 \end{cases}$$

which is zero because

$$(1+P_{i,l})\psi_2 = (1+P_{l,k})\psi_2 = 0$$

2. When $i,j \neq k$, the anti-symmetry condition after the vertical line is obviously satisfied. When $j = k$ we have

$$(1+P_{i,k})\Psi_2 = -\sum_{t\neq 1} P_{t,k}\left[1-\sum_{i} P_{l,n+1}+(n-2k+2)P_{k,n+1}\right](1+P_{t,i})\psi_2 F_2$$

which is equal to zero because

$$(1+P_{t,i})\psi_2 = 0$$

3. The cyclic symmetry condition may be verified by using the properties of $\psi_2$. After some transformations we have

$$\left(1-\sum_{j=k+1}^{n+1} P_{k,j}\right)\Psi_2 = \left(1+\sum_{j=k}^{n} P_{j,n+1}\right)\left[\left(1-\sum_{j=k+1}^{n} P_{k,j}\right) - \sum_{t=1}^{k-1} P_{t,k}\left(1-\sum_{j=k+1}^{n} P_{t,j}\right) - (n-2k+2)\right]\psi_2 F_2$$

Next, it may be shown that

$$\left[\left(1-\sum_{j=k+1}^{n} P_{k,j}\right) - \sum_{t=1}^{k-1} P_{t,k}\left(1-\sum_{j=k+1}^{n} P_{t,j}\right)\right]\psi_2 = (n-2k+2)\psi_2$$

and therefore

$$\left(1-\sum_{j=k+1}^{n+1} P_{k,j}\right)\Psi_2 = 0$$

From the general formulae (30.8) and (30.9) we have, as a special case of the expression used in § 24,

$$\Psi_1(1|23) = \frac{1}{\sqrt{2}}[\psi(1|2)F(3) - \psi(1|3)F(2)]$$

$$\Psi_2(1|23) = \frac{1}{\sqrt{6}}[\psi(|12)F(3) - \psi(|13)F(2) + 2\psi(|32)F(1)]$$

We can use the above results to write down an expression for the coordinate function of the atom + electron system in terms of the atomic and one-electron functions. Let $A$ be the set of numbers indicating the energy of the atom, its orbital angular momentum and the $z$-component of the angular momentum. We shall write $\Psi$ as the sum

$$\Psi = \sum_{A} (\Psi_{A1} + \Psi_{A2}) \tag{30.11}$$

Each of the terms $\Psi_{A1,2}$ will consist of expressions of the form of (30.8) or (30.9).

If we omit the common factor of $\Psi_{A1,2}$, which will be unimportant in the ensuing analysis, we have

$$\Psi_{A1} = \left(1-\sum_{i=k+1}^{n} P_{i,n+1}\right)\psi_{A1}F_{A1}$$

$$\Psi_{A2} = \left(\sqrt{k\frac{(n-2k+2)^2}{n-k+1}} + k\right)^{-1}\left(1-\sum_{t=1}^{k-1} P_{t,k}\right) \times \left[1-\sum_{i=k+1}^{n} P_{i,n+1} + (n-2k+2)P_{k,n+1}\right]\psi_2 F_{A2} \tag{30.12}$$

## 31. EQUATIONS FOR THE FUNCTIONS $F_{Aa}$

In order to establish the equations for $F_{Aa}$, we shall use a relation analogous to (10.24), i.e.

$$\int \psi_{Aa}^{*}(H-\mathscr{E})\Psi\, dr_1, \ldots, dr_n = 0, \qquad a = 1, 2 \tag{31.1}$$

in which $H$ is the energy operator for the electron + atom system.

We shall suppose that $\psi_{Aa}^*$ is the exact atomic function so that

$$(H_0 - E_{Aa})\psi_{Aa} = 0 \tag{31.2}$$

The exact functions will be replaced by the approximate atomic functions only in the final expressions which will be of the density-matrix type.

There is another way of deriving the equations for $F_{Aa}$ [92, 93], in which it is supposed from the outset that $\psi_{Aa}$ are the functions for the self-consistent field.

Let us now write the energy operator for the atom + electron system in the form

$$H = H_0 - \tfrac{1}{2}\Delta_{n+1} + V(r_1, \ldots, r_{n+1}) \tag{31.3}$$

where $V$ is the energy of interaction of the $(n+1)$th electron with the nucleus and the remaining $n$ electrons; it is given by

$$V = -\frac{z}{r_{n+1}} + \sum_{i=1}^{n} \frac{1}{|r_{n+1} - r_i|} \tag{31.4}$$

Substituting the expression for $\Psi$ and $H$ given by (30.11), (30.12) and (31.3), (31.1) and using the orthogonality and symmetry of $\psi$, we have, in view of (31.2)

$$(\Delta + k_{Aa}^2)F_{Aa} = 2\sum_{A'} V_{AA'a}F_{A'a} + \sum_{A'a'} \hat{W}_{AA'aa'}F_{A'a'} \tag{31.5}$$

where

$$V_{AA'a}(r_{n+1}) = \int \psi_{Aa}^* V \psi_{A'a}\, dr_1, \ldots, dr_n \tag{31.6}$$

is the interaction energy matrix,

$$k_{Aa}^2 = 2(\mathscr{E} - E_{Aa}) \tag{31.7}$$

and $\hat{W}$ is the exchange operator of the form

$$\begin{aligned}\hat{W}_{AA'aa'}F_{A'a'}(r_{n+1}) = p_{aa'} &\int \psi_{Aa}^*(r_1, \ldots | \ldots, r_n)(\Delta_1 + k_{A'a}^2 - 2V)\\ &\times \psi_{A'a'}(r_{n+1}, \ldots | \ldots, r_n)F_{A'a'}(r_1)\, dr_1, \ldots, dr_n\\ &+ q_{aa'} \int \psi_{Aa}^*(r_1, \ldots | \ldots, r_n)(\Delta_n + k_{A'a}^2 - 2V)\\ &\times \psi_{A'a'}(r_1, \ldots | \ldots, r_{n+1})F_{A'a'}(r_n)\, dr_1, \ldots, dr_n\end{aligned} \tag{31.8}$$

$p_{aa'}$ and $q_{aa'}$ are given by

$$\begin{aligned}p_{11} &= p_{12} = p_{21} = 0\\ p_{22} &= (k-1)(n-2k+3)(n-2k+2)^{-1}\\ q_{11} &= n - k\\ q_{12} &= k^{\frac{1}{2}}(n-k)(n-2k+3)(n-k+1)^{\frac{1}{2}}[(n-2k+2)^2 + n - k + 1]^{-\frac{1}{2}}\\ q_{21} &= (n-k)k^{\frac{1}{2}}\left[1 + \frac{n-k+1}{(n-2k+2)^2}\right]^{\frac{1}{2}}\\ q_{22} &= -(n-k+1)(n-2k+2)^{-1}\end{aligned} \tag{31.9}$$

Using the explicit expression for $V$, the symmetry properties of $\psi_{Aa}$ and the fact that $\Delta$ is self-adjoint, the potential energy matrix and the exchange operator may be reduced to the forms

$$V_{AA'a} = \left[ -\frac{z}{r} + \int \frac{\rho_{AA'a}(\boldsymbol{r}')\,d\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|} \right] \tag{31.10}$$

$$\hat{W}_{AA'aa'}F_{A'a'} = \int W_{AA'aa'}(\boldsymbol{r}',\boldsymbol{r})F_{A'a'}(\boldsymbol{r}')\,d\boldsymbol{r}' \tag{31.11}$$

$$W_{AA'aa'}(\boldsymbol{r}',\boldsymbol{r}) = \left(\tfrac{1}{2}\Delta' + \tfrac{1}{2}k_{A'a}^2 + \frac{z}{r'} - \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\right)\rho_{AA'aa'}(\boldsymbol{r}',\boldsymbol{r}) - \int \frac{\rho_{AA'aa'}(\boldsymbol{r}'',\boldsymbol{r}',\boldsymbol{r})}{|\boldsymbol{r}''-\boldsymbol{r}'|}\,d\boldsymbol{r}'' \tag{31.12}$$

where the $\rho$ represent expressions of the density-matrix type.

In order to write these expressions in the most compact form, we shall introduce a special symbol for the integral of the product $\psi_{Aa}^{*}\psi_{A'a'}$ over all the variables with the exception of a specified few. For example, the integral with respect to all the variables $r_1, \ldots, r_n$ except for $r_i$ will be denoted by the symbol

$$(r_i)_{Aa}(r_i)_{A'a'} = \int \psi_{Aa}^{*}\psi_{A'a'}\,d\boldsymbol{r}_1, \ldots, d\boldsymbol{r}_{i-1}\,d\boldsymbol{r}_{i+1}, \ldots, d\boldsymbol{r}_n \tag{31.13}$$

If, after integration, $r_i$ in $\psi_{Aa}$ is replaced by, say, $r$, while in $\psi_{A'a'}$ it is replaced by $r'$, this will be denoted by

$$\binom{r}{r_i}_{Aa}\binom{r'}{r_i}_{A'a'}$$

In this notation we have

$$\rho_{AA'1}(\boldsymbol{r}') = k\binom{r'}{r_n}_{A1}\binom{r'}{r_1}_{A'1} + (n-k)\binom{r'}{r_n}_{A1}\binom{r'}{r_n}_{A'1} \tag{31.14}$$

$$\rho_{AA'2}(\boldsymbol{r}') = (k-1)\binom{r'}{r_1}_{A2}\binom{r}{r_n}_{A'2} + (n-k+1)\binom{r'}{r_n}_{A2}\binom{r'}{r_n}_{A'2} \tag{31.15}$$

$$\rho_{AA'11}(\boldsymbol{r}',\boldsymbol{r}) = q_{11}\binom{r'}{r_n}_{A1}\binom{r}{r_n}_{A'1} \tag{31.16}$$

$$\rho_{AA'12}(\boldsymbol{r}',\boldsymbol{r}) = q_{12}\binom{r'}{r_n}_{A1}\binom{r}{r_n}_{A'2} \tag{31.17}$$

$$\rho_{AA'21}(\boldsymbol{r}',\boldsymbol{r}) = q_{21}\binom{r'}{r_n}_{A2}\binom{r}{r_n}_{A'1} \tag{31.18}$$

$$\rho_{AA'22}(\boldsymbol{r}',\boldsymbol{r}) = q_{22}\binom{r'}{r_n}_{A2}\binom{r}{r_n}_{A'2} + p_{22}\binom{r'}{r_1}_{A2}\binom{r}{r_1}_{A'2} \tag{31.19}$$

$$\rho_{AA'11}(\boldsymbol{r}'',\boldsymbol{r}',\boldsymbol{r}) = q_{11}\left[k\begin{pmatrix} r'' & r' \\ r_n & r_n \end{pmatrix}_{A1}\begin{pmatrix} r'' & r \\ r_n & r_n \end{pmatrix}_{A'1} + (n-k-1)\begin{pmatrix} r'' & r' \\ r_{n-1} & r_n \end{pmatrix}_{A1}\begin{pmatrix} r'' & r \\ r_{n-1} & r_n \end{pmatrix}_{A'1}\right] \tag{31.20}$$

$$\rho_{AA'12}(r'',r',r) = q_{12}\left[(k-1)\begin{pmatrix} r'' & r' \\ r_1 & r_n\end{pmatrix}_{A1}\begin{pmatrix} r'' & r \\ r_1 & r_n\end{pmatrix}_{A'2} + \begin{pmatrix} r'' & r' \\ r_k & r_n\end{pmatrix}_{A1}\begin{pmatrix} r'' & r' \\ r_k & r_n\end{pmatrix}_{A'2} + (n-k-1)\begin{pmatrix} r'' & r' \\ r_{n-1} & r_n\end{pmatrix}_{A1}\begin{pmatrix} r'' & r \\ r_{n-1} & r_n\end{pmatrix}_{A'2}\right] \tag{31.21}$$

$$\rho_{AA'21}(r'',r',r) = q_{21}\left[(k-1)\begin{pmatrix} r'' & r' \\ r_1 & r_n\end{pmatrix}_{A2}\begin{pmatrix} r'' & r \\ r_1 & r_n\end{pmatrix}_{A'1} + \begin{pmatrix} r'' & r' \\ r_k & r_n\end{pmatrix}_{A2}\begin{pmatrix} r'' & r \\ r_k & r_n\end{pmatrix}_{A'1} + (n-k-1)\begin{pmatrix} r'' & r' \\ r_{n-1} & r_n\end{pmatrix}_{A2}\begin{pmatrix} r'' & r \\ r_{n-1} & r_n\end{pmatrix}_{A'1}\right] \tag{31.22}$$

$$\begin{aligned}\rho_{AA'22}(r'',r',r) = q_{22}&\left[(k-1)\begin{pmatrix} r'' & r' \\ r_1 & r_n\end{pmatrix}_{A2}\begin{pmatrix} r'' & r \\ r_1 & r_n\end{pmatrix}_{A'2} + (n-k)\begin{pmatrix} r'' & r' \\ r_{n-1} & r_n\end{pmatrix}_{A2}\begin{pmatrix} r'' & r \\ r_{n-1} & r_n\end{pmatrix}_{A'2}\right] \\ &+ p_{22}\left[(k-2)\begin{pmatrix} r' & r'' \\ r_1 & r_2\end{pmatrix}_{A2}\begin{pmatrix} r & r'' \\ r_1 & r_2\end{pmatrix}_{A'2} + (n-k+1)\begin{pmatrix} r' & r'' \\ r_1 & r_n\end{pmatrix}_{A2}\begin{pmatrix} r & r'' \\ r_1 & r_n\end{pmatrix}_{A'2}\right]\end{aligned} \tag{31.23}$$

Using the expression for the exchange operator we can reduce (31.5) to

$$(\Delta + k_{Aa}^2)F_{Aa} = 2\sum_{A'} V_{AA'a}F_{A'a} + 2\sum_{A'a'}\int W_{AA'aa'}(r',r)F_{A'a'}(r')\,dr' \tag{31.24}$$

The asymptotic expression for $F_{Aa}$ in the case of a collision with a neutral atom is

$$F_{Aa} \sim e^{ik_{Aa}r}\delta_{Aa,A_0a_0} + q_{A_0a_0Aa}\frac{e^{ik_{Aa}r}}{r} \tag{31.25}$$

while in the case of a collision with an ion it is

$$F_{Aa} \sim e^{i\left[k_{Aa}r + \frac{Z_0}{k_{Aa}}\ln(k_{Aa}r - k_{Aa}r)\right]} + q_{A_0a_0Aa}\frac{1}{r}e^{i\left(k_{Aa}r + \frac{Z_0}{k_{Aa}}\ln 2k_{Aa}r\right)} \tag{31.26}$$

where $k_{Aa} = k_{Aa}v$.

The system of integro-differential equations (31.24) subject to the asymptotic conditions (31.25) or (31.26) may be transformed to a system of integral equations. Let $G_{Aa}$ be the Green's function which in the case of a collision with a neutral atom is of the form

$$G_{Aa} = -\frac{1}{2\pi}\frac{e^{ik_{Aa}|r-r'|}}{|r-r'|} \tag{31.27}$$

while in the case of a collision with an ion of charge $Z$ it satisfies the equation

$$\left(\tfrac{1}{2}\Delta + \tfrac{1}{2}k_{Aa}^2 + \frac{Z}{r}\right)G_{Aa} = -\delta(r-r') \tag{31.28}$$

By analogy with (10.53), consider the kernel

$$K_{AA'aa'} = -G_{Aa}(\mathbf{r},\mathbf{r}')\left(V_{AA'a} - \frac{Z}{r}\delta_{AA'}\right)\delta_{aa'} - \int G_{Aa}(\mathbf{r},\mathbf{r}'')W_{AA'aa'}(\mathbf{r}'',\mathbf{r}')\,d\mathbf{r}'' \tag{31.29}$$

(in the case of collisions with neutral atoms $Z = 0$). We then have

$$F_{Aa} = \varphi_{Aa}\delta_{AA_0}\delta_{aa_0} + \sum_{A'a'}\int K_{AA'aa'}(\mathbf{r},\mathbf{r}')F_{A'a'}(\mathbf{r}')\,d\mathbf{r}' \tag{31.30}$$

where $\varphi_{Aa}$ represents either $\exp(ik_{Aa}\mathbf{r})$ in the case of collision with a neutral atom, or else the Coulomb function with the asymptotic behaviour

$$\varphi_{Aa} \sim e^{i\left[k_{Aa}\mathbf{r} + \frac{Z}{k_{Aa}}\ln(k_{Aa}r - k_{Aa}\mathbf{r})\right]} + q^{(0)}_{AaAa}\frac{e^{i\left(k_{Aa}r + \frac{Z}{k_{Aa}}\ln 2k_{Aa}r\right)}}{r} \tag{31.31}$$

It is known [57] that this function can also be written in the form

$$\varphi = e^{\frac{\pi Z}{2k}}\Gamma\left(1 - i\frac{Z}{k}\right)e^{ik\mathbf{r}}F\left[\frac{iZ}{k}, 1, i(kr - k\mathbf{r})\right] \tag{31.32}$$

where $F$ is the degenerate hypergeometric function.

From equation (31.30) it is possible to obtain the expression for the amplitude $q_{A_0a_0Aa}$. One must consider the asymptotic behaviour at large $\mathbf{r}$. The Green's function $G_{Aa}(\mathbf{r},\mathbf{r}')$ for large $\mathbf{r}$ and finite $\mathbf{r}'$ has the following asymptotic properties: for collisions with neutral atoms

$$G \sim -\frac{1}{4\pi}\frac{e^{ik_{Aa}r}}{r}e^{-ik_{Aa}\mathbf{r}'} \tag{31.33}$$

whereas for collisions with ions

$$G \sim -\frac{1}{4\pi}e^{i\left(k_{Aa}r + \frac{Z}{k_{Aa}}\ln 2k_{Aa}r\right)}\tilde{\varphi}_{Aa} \tag{31.34}$$

where

$$\tilde{\varphi} = e^{\frac{\pi Z}{2k}}\Gamma\left(1 + i\frac{Z}{k}\right)e^{ik_{Aa}\mathbf{r}'}F\left[-\frac{iZ}{k}, 1, -i(kr + k\mathbf{r})\right] \tag{31.35}$$

Substituting (31.33) or (31.34) into (31.30) and bearing in mind (31.25) and (31.26) we have for collisions with neutral atoms:

$$\begin{aligned} q_{A_0a_0Aa} = -\frac{1}{2\pi}\sum_{A'a'}\int e^{ik_{Aa}\mathbf{r}'}\Big[\delta_{aa'}V_{AA'a}F_{A'a'}(\mathbf{r}'') \\ + \int d\mathbf{r}''\,W_{AA'aa'}(\mathbf{r}',\mathbf{r}'')F_{A'a'}(\mathbf{r}'')\Big]\,d\mathbf{r}' \end{aligned} \tag{31.36}$$

and for collisions with ions:

$$\begin{aligned} q_{A_0a_0Aa} = -\frac{1}{2\pi}\sum_{A'a'}\int \tilde{\varphi}_{Aa}(\mathbf{r}')\Big[V_{AA'a}\delta_{aa'}F_{A'a'}(\mathbf{r}') \\ + \int W_{AA'aa'}(\mathbf{r}',\mathbf{r}'')F_{A'a'}(\mathbf{r}'')\,d\mathbf{r}''\Big]\,d\mathbf{r}' + q^{(0)}_{A_0a_0A_0a_0}\delta_{AA_0}\delta_{aa_0} \end{aligned} \tag{31.37}$$

Consider the asymptotic form of the complete wave function, including the spin variables. By analogy with § 25, we shall separate out the terms which are finite when, say, $r_{n+1} \to \infty$ (we shall therefore be concerned with that part of (30.11) which contains the atomic functions for the discrete spectrum). After some transformations

$$\Phi \sim \sum_A \Phi_{A1} F_{A1}(r_{n+1})\alpha_{n+1} + \frac{\sqrt{n-k+1}}{\sqrt{(n-2k+2)^2+n-k+1}} \sum_A \Phi'_{A2} F_{A2}(r_{n+1})\alpha_{n+1}$$
$$- \frac{n-2k+2}{\sqrt{(n-2k+2)^2+n-k+1}} \sum_A \Phi_{A2} F_{A2}(r_{n+1})\beta_{n+1} \qquad (31.38)$$

where a numerical factor has been omitted. In these expressions, $\Phi_{A1}$ is the atomic wave function with spin $s-\frac{1}{2}$ made up in accordance with (24.6) from $\psi_{A1}$ and $\chi = \beta_1, \ldots, \beta_k, \alpha_{k+1}, \ldots, \alpha_n$; $\Phi_{A2}$ is the atomic wave function with spin $s+\frac{1}{2}$ made up in accordance with (24.6) from $\psi_{A2}$ and $\chi = \beta_1, \ldots, \beta_{k-1}, \alpha_k, \ldots, \alpha_n$; and $\Phi'_{A2}$ is made up in accordance with (24.6), also from $\psi_{A2}$, but with $\chi$ given by

$$\chi = (n-k+1)^{-\frac{1}{2}}\left(1+\sum_{j=k+1}^{n} P_{k,j}\right)\beta_1, \ldots, \beta_k, \alpha_{k+1}, \ldots, \alpha_n$$

($\Phi'_{A2}$ corresponds to spin $s+\frac{1}{2}$ but the spin $z$-component for this function is $s-\frac{1}{2}$ and not $s+\frac{1}{2}$).

As an example, consider the collision of an electron with an atom whose spin prior to the collision is zero. In view of (30.3) we have from (31.36)

$$\Phi \sim \Phi_{A_01} e^{ik_{A_01}r}\alpha + \sum_A \Phi_{A1} q_{A_01A1}\frac{e^{ik_{A1}r}}{r}\alpha + \sqrt{\frac{k+1}{k+5}} \sum_A \Phi'_{A2} q_{A_01A2}\frac{e^{ik_{A2}r}}{r}\alpha$$
$$- \sqrt{\frac{4}{k+5}} \sum_A \Phi_{A2} q_{A_01A2}\frac{e^{ik_{A2}r}}{r}\beta \qquad (31.39)$$

where we have omitted the subscript $n+1$. Hence, when there is no change in the spin of the atom, the differential cross-section is

$$d\sigma_{A_01A1} = \frac{k_{A1}}{k_{A_01}}\left|q_{A_01A1}\right|^2 d\Omega \qquad (31.40)$$

while if the spin change is allowed, we have on summing over the final spin states

$$d\sigma_{A_01A2} = \frac{k_{A2}}{k_{A_01}}\left|q_{A_01A2}\right|^2 d\Omega \qquad (31.41)$$

If the atom has a non-zero spin, say, $s_0$, prior to collision, there are two possible values for the spin of the system, namely, $s_1 = s_0+\frac{1}{2}$ and $s_2 = s_0-\frac{1}{2}$. This leads to two different problems. In one of them the initial state of the atom is described by a function $\Phi_{A_01}$ while in the other it is described by $\Phi_{A_02}$. In order to obtain the observed cross-section, the result must be averaged over the spins. Considerable simplification is achieved by considering the valency electrons of the atom and the incident electron as moving in the field of the nucleus, and fixing all the internal electrons. In this approximation we shall use the symmetrized function for the system consisting of the valency electrons of the atom plus the incident electron. The simplest example of this kind is the monovalent atom. According to V. A. Fock, the wave function for the valency electron satisfies the equation

$$[-\tfrac{1}{2}\Delta+U(r)]\psi_\alpha+\hat{W}\psi_\alpha = E_\alpha\psi_\alpha \tag{31.42}$$

where $U$ is the potential energy of interaction of the valency electrons with the nucleus and the inner electrons and is given by

$$U = -\frac{Z}{r}+\int\frac{2\rho(r,r')}{|r-r'|}dr' \tag{31.43}$$

while $\hat{W}$ is the exchange operator defined by

$$\hat{W}\psi_\alpha = \int\frac{\rho(r,r')\psi_\alpha(r')}{|r-r'|}dr' \tag{31.44}$$

Equation (31.32) may be written in the shorter form

$$H_F\psi_\alpha = E_\alpha\psi_\alpha \tag{31.45}$$

The coordinate part of the wave function for the system consisting of the valency electron plus the incident electron will satisfy the equation

$$\left[H_F(r)+H_F(r')+\frac{1}{|r-r'|}\right]\Psi = E\Psi \tag{31.46}$$

By analogy with (10.46) we shall write $\Psi$ in the form

$$\Psi = \sum_\alpha [F_\alpha(r)\psi_\alpha(r')\pm F_\alpha(r')\psi_\alpha(r)] \tag{31.47}$$

From

$$\int\psi_\alpha(r)\left[H_F(r)+H_F(r')+\frac{1}{|r-r'|}\right]\Psi(r,r')\,dr' = 0$$

we have the following equation for $F_\alpha$

$$\left(H_F-\frac{k_\alpha^2}{2}\right)F_\alpha(r)+\sum_{\alpha'}V_{\alpha\alpha'}F_{\alpha'}(r)+\sum_{\alpha'}\int W_{\alpha\alpha'}(r',r)F_{\alpha'}(r')\,dr' = 0 \tag{31.48}$$

where

$$V_{\alpha\alpha'} = \int\frac{\psi_\alpha^*(r')\psi_{\alpha'}(r')}{|r-r'|}dr' \tag{31.49}$$

$$W_{\alpha\alpha'} = \pm\left(E_{\alpha'}-\tfrac{1}{2}k_\alpha^2+\frac{1}{|r-r'|}\right)\psi_\alpha^*(r)\psi_{\alpha'}(r') \tag{31.50}$$

The operator $W_{\alpha\alpha'}$ describes the exchange interaction between the incident electron and the valency electron. The exchange interaction with the inner electrons is described by the operator $\hat{W}$ in $H_F$.

If we let $F$ have the asymptotic form

$$F_\alpha \sim e^{ik_\alpha r}\,\delta_{\alpha\alpha_0} + q^{\pm}_{\alpha_0\alpha}\frac{e^{ik_\alpha r}}{r} \tag{31.51}$$

then by analogy with the case of the hydrogen atom, the scattering cross-section assumes the form

$$d\sigma^{\pm} = \left|q^{\pm}_{\alpha_0\alpha}\right|^2 d\Omega \tag{31.52}$$

Separation of the angular variables in (31.24) or (31.48) is carried out exactly as in the case of a collision of an electron with a hydrogen atom (§ 11).

The equations for the partial waves are of the form

$$\frac{d^2}{dr^2} f_{Aal} + \left[k^2_{Aa} - \frac{l(l+1)}{r^2}\right] f_{Aal} = 2\sum_{A'l'} \mathscr{V}_{AA'all'} f_{A'a'l'} + 2\sum_{A'a'l'} \int_0^\infty \mathscr{W}_{AA'aa'll'}(r', r) f_{A'a'l'}(r')\,dr' \tag{31.53}$$

where $\mathscr{V}_{AA'all'}$ and $\mathscr{W}_{AA'aa'll'}$ are given in terms of $V_{AA'aa}$ and $W_{AA'aa'}$ by

$$\mathscr{V}_{AA'all'} = \int Y_{l\mu}(0'\varphi') V_{AA'a}(r') Y_{l'\mu'}(0'\varphi')\,d\Omega \tag{31.54}$$

$$\mathscr{W}_{AA'aa'll'}(r', r'') = r'r'' \int Y^*_{l\mu}(0''\varphi'') W_{AA'aa'}(r', r'') Y_{l'\mu'}(0'\varphi')\,d\Omega'\,d\Omega'' \tag{31.55}$$

Owing to the presence of the term $|r' + r''|^{-1}$ in $W_{AA'aa'}(r', r'')$, the expression given by (31.55) will be different for $r < r'$ and $r > r'$. The two cases will be represented by $\mathscr{W}^{(1)}$ and $\mathscr{W}^{(2)}$, respectively. The exchange term on the right-hand side of (31.53) may be written in the form

$$\int_0^\infty \mathscr{W}_{\nu\nu'} f_{\nu'}\,dr' = \int_0^r (\mathscr{W}^{(1)}_{\nu\nu'} - \mathscr{W}^{(2)}_{\nu\nu'}) f_{\nu'}\,dr' + \int_0^\infty \mathscr{W}^{(2)}_{\nu\nu'} f_{\nu'}\,dr' \tag{31.56}$$

where $\nu$ represents the group of subscripts $Aal$. Equation (31.53) cannot readily be solved numerically because of the presence of the integral $\int_0^\infty \mathscr{W}^{(2)}_{\nu\nu'} f_{\nu'}\,dr'$, and successive iterations are necessary. However, if we use approximate atomic functions which are expressed in terms of the one-electron functions, we can write

$$\mathscr{W}^{(2)}_{\nu\nu'} = \sum_i R_{i\nu\nu'}(r) Q_{i\nu\nu'}(r') \tag{31.57}$$

This may be used as in § 14 in order to transform equation (31.53) into a form which can be solved without iteration.

## Chapter 9

# COLLISION OF AN ELECTRON WITH A SODIUM ATOM

### 32. Elastic Scattering of Electrons by Sodium Atoms

As an example of the application of the general theory developed in the preceding chapter, let us consider one of the simplest problems, the collision of an electron with a sodium atom. In accordance with the discussion in § 31 this problem may be looked upon as involving the motion of two electrons, i.e. the incident and the valency electrons in the field of the nucleus and of the inner electrons. The latter comprise ten electrons in the $1s$, $2s$ and $2p$ shells.

Among existing calculations of the inelastic scattering of electrons by sodium atoms, the most accurate is that reported in [94]. This work is concerned with the scattering length, making allowance for exchange and $3s-3p$ coupling. It turns out that this coupling plays a very important role. Using experimental data on oscillator strengths, the authors of this paper conclude that 99·4% of the polarizability of the atom is due to the $3s-3p$ coupling. Therefore, when the single virtual transition $3s-3p$ is included, this accounts almost completely for the polarization of the atom by the incident electron.

The equations discussed in [94] are, in fact, identical with (31.48), although they are derived in a different way. The corresponding equations for the partial waves on the total angular momentum representation are of the form

$$(H_F^{(l_2)}-\tfrac{1}{2}k_{nl_1}^2)f_{\nu L}+\sum_{\nu'}\mathscr{V}_{\nu\nu' L}f_{\nu' L}+\sum_{\nu'}\int_0^\infty \mathscr{W}_{\nu\nu' L}f_{\nu' L}\,dr'=0 \qquad (32.1)$$

$$H_F^{(l)}=-\frac{1}{2}\frac{d^2}{dr^2}+\frac{1}{2}\frac{l(l+1)}{r^2}+U(r)+\hat{W}f \qquad (32.2)$$

and $\nu=(n,\, l_1,\, l_2)$

The function $U(r)$ and the exchange operator $\hat{W}f$ can be expressed in terms of the densities $\rho(r, r)$ and $\rho(r, r')$ constructed from wave functions for the closed shells using (31.33) and (31.34). In the present case

$$\rho(\mathbf{r},\mathbf{r}')=\frac{1}{4\pi}R_{1s}(r)R_{1s}(r')+\frac{1}{4\pi}R_{2s}(r)R_{2s}(r')$$
$$+\sum_{\mu=-1}^{1}R_{2p}(r)R_{2p}(r')Y_{1\mu}^{*}(\theta,\varphi)Y_{1\mu}(\theta',\varphi') \qquad (32.3)$$

where $R_{1s}$, $R_{2s}$ and $R_{2p}$ are the radial wave functions for the atomic electrons in the closed shells.

Using (32.3), we have the following expressions for $U$ and $\hat{W}$

$$U = -\frac{11}{r} + 2\int\limits_0^\infty (R_{1s}^2 + R_{2s}^2 + 3R_{2p}^2)\gamma_0(r, r')r'^2\,dr' \tag{32.4}$$

$$\begin{aligned} \hat{W}F = \frac{1}{2l+1}\Bigg\{ & \int\limits_0^\infty \gamma_{l_2}(r, r')r'R_{1s}(r')F(r')\,dr'\,R_{1s}(r) \\ & + \int\limits_0^\infty \gamma_{l_2}(r, r')r'R_{2s}(r')F(r')\,dr'\,R_{2s}(r) \\ & + \frac{3l_2}{2l_2-1}\int\limits_0^\infty \gamma_{l_2-1}(r, r')R_{2p}(r')F(r')\,dr'\,R_{2p}(r) \\ & + \frac{(3l_2+3)}{(2l_2+3)}\int\limits_0^\infty \gamma_{l_2+1}(r, r')r'R_{2p}(r')F(r')\,dr'\,R_{2p}(r)\Bigg\} \end{aligned} \tag{32.5}$$

where

$$\gamma_l = \begin{cases} \dfrac{r}{r'^{l+1}} & r \leqslant r' \\[2ex] \dfrac{r'^l}{r^{l+1}} & r' \leqslant r \end{cases}$$

The quantities $\mathscr{V}_{vv'L}$ and $\mathscr{W}_{vv'L}$ which enter into (32.1) can be expressed in terms of the wave functions for the valency electron in the ground $3s$ state or the excited states.

As was pointed out above, calculations of the scattering length can, in practice, be confined to the single $3p$ excited state.

The wave functions for the electrons in the closed shells $R_{1s}$, $R_{2s}$ and $R_{2p}$ and the function for the valency electron in the $3s$ and $3p$ states were taken from [95, 96].

The system of equations given by (32.1) can, on the present approximation, be reduced to two equations for $f_{300,0}$ and $f_{311,0}$ (the subscript $A$ which characterizes the state of the atom is now replaced by the triad of quantum numbers $n$, $l$, $\mu$). In order to find the scattering length we must set $k_{30}^2 = 0$. We then have $k_{31}^2 = -\kappa^2 = -0{\cdot}137$. The asymptotic behaviour of $f_{300,0}$ and $f_{311,0}$ as $r \to \infty$ is

$$f_{300,0}(r) \sim r - a^{\pm}; \qquad f_{311,0} \sim e^{-\chi r} \tag{32.6}$$

In [91] the equations for $f_{300,0}$ and $f_{311,0}$ were solved by the method of successive approximations. At first the exchange operator $\hat{W}$ was neglected in the operator $H_F$ so that $H_F$ became the energy operator $H_c$ on the central field approximation. The exchange term $\int_0^\infty \mathscr{W} f \, dr'$ was also neglected. The zero-order approximation, $f^{(0)}$, to the functions $f$ was then substituted into the exchange term.

The solution of the equations with the exchange term $\int_0^\infty \mathscr{W} f^{(0)} \, dr$ gave the first approximation $f^{(1)}$ which was again substituted for $f$ in the exchange term, and so on. The values of $a^+$ and $a^-$ given in Table 16 were obtained after five successive approximations ($n$ represents the order of the approximation).

TABLE 16

| $n$ | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| $a^+$ | −2·4 | 10·0 | 14·0 | 13·9 | — |
| $a^-$ | −2·4 | −9·6 | −5·3 | −9·5 | −6·6 |

Next, the effect of the exchange interaction with the 1*s* and 2*s* shell on the function $f_{300,0}$ was determined in a similar way by substituting the function $f^{(0)}_{300,0}$ into the operator $\hat{W} f$.

The final values of $a^{\pm}$ were found to be $a^+ = 12$, $a^- = -9$. The cross-section averaged over the spins could be determined from known $a^+$ and $a^-$:

$$\langle \sigma \rangle = \pi[3(a^-)^2 + (a^+)^2]$$

It was found to be $380\pi a_0^2$. Moreover, it is possible to use these values of $a^+$ and $a^-$ to determine the amplitude when the scattering process is accompanied by the spin flip of the valency electron.

$$\text{Na}(\uparrow) + e(\downarrow) = \text{Na}(\downarrow) + e(\uparrow)$$

Let $\mu_{s1}$ and $\mu_{s2}$ be the spin $z$-components of the valency and incident electrons respectively. Spin flip involves the transition

$$(\mu_{s1}, \mu_{s2}) \rightarrow -(\mu_{s1}, -\mu_{s2}) \tag{32.7}$$

Since $\mu_{s1} + \mu_{s2}$ must be conserved, this transition can only occur when $\mu_{s1} + \mu_{s2} = 0$.

Let us express the scattering length $a(\mu_{s1}, \mu_{s2}, -\mu_{s1}, -\mu_{s2})$ for the process defined by (32.7) in terms of $a^+$ and $a^-$. Instead of the symbols + and − we shall write (0) and (1) in accordance with the magnitude of the total spin. We then have

$$a(\mu_{s1}, -\mu_{s1}, -\mu_{s1}, \mu_{s1}) = \sum_s C^{s0}_{\frac{1}{2} - \mu_{s1} \frac{1}{2} \mu_{s1}} a^{(s)} C^{s0}_{\frac{1}{2} - \mu_{s1} \frac{1}{2} \mu_{s1}} \tag{32.8}$$

Substituting the values of the Clebsch-Gordan coefficients we obtain

$$a(\mu_{s1}, -\mu_{s1}, -\mu_{s1}, \mu_{s1}) = \tfrac{1}{2}(a^{(1)} - a^{(0)}) \tag{32.9}$$

The corresponding effective cross-section is $\sigma = 440\pi a_0^2$, which is consistent with the experimental result $\sigma \geqslant 260\pi a_0^2$ [97].

## 33. EXCITATION OF THE SODIUM ATOM

The excitation of the $3p$ level of sodium was considered in [94] on the modified Born approximation (§ 18). In the equations for the partial waves, only the matrix element $V_{n,l_1,l_2;n',l_1',l_2'}$ was taken into account, i.e. the $3s-3p$ interaction. In this matrix element only the dipole part was retained. The latter is proportional to

$$(\gamma_1)_{3s,3p} = \frac{1}{r^2}\int_0^r R_{3s}R_{3p}r^3\,dr + \int_r^\infty R_{3s}R_{3p}r\,dr \tag{33.1}$$

This quantity was then replaced by its asymptotic form

$$(\gamma)_{3s,3p} \sim \frac{1}{r^2}\int_0^\infty R_{3s}R_{3p}r^3\,dr \tag{33.2}$$

It would appear that only the long range part of the interaction was taken into account in this particular calculation. However, this long range part plays the dominating role in the case under consideration.

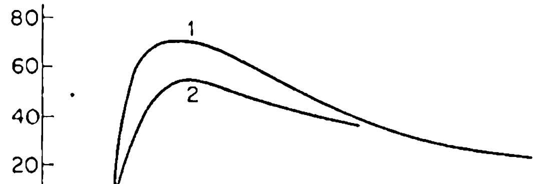

FIG. 46. Cross-section for the excitation of the $3p$-state of the sodium atom (in units of $\pi a_0^2$): 1—calculated, 2—experimental

Figure 46 shows the numerical results of the calculation and the experimental data as given in [94].

## *Chapter 10*

# EXCITATION OF MULTIPLY-CHARGED IONS

### 34. Excitation of the 2*s* and 3*s* States of Hydrogen-like Ions

When an electron collides with a multiply-charged ion, the unscreened Coulomb field has a considerable effect on the electron. It is then convenient to use an approximation in which the Coulomb field is taken into account exactly, whereas the effect of the electrons in the electron shell is regarded as a small perturbation. This approximation involves the replacement of $F_{A'a'}$ in (31.37) by $\varphi_{A'a'}$. If, in addition, the exchange interaction is also neglected, then the excitation amplitude becomes

$$q_{A_0A} = -\frac{1}{2\pi}\int \tilde{\varphi}_A V_{AA_0}\varphi_{A_0}\,dr \tag{34.1}$$

Calculations based on this formula were carried out in [98] for transitions to the 2*s* and 3*s* states in hydrogen-like ions and for optically allowed transitions on the dipole approximation.

Let us consider the excitation of hydrogen-like ions. The matrix element $V_{Aa_0}$ is then given by

$$V_{AA_0} = \int \frac{\psi_{A_0}^*\psi_A}{|r-r'|}\,dr' \tag{34.2}$$

where $\psi_{A_0}$ and $\psi_A$ are the wave functions for the initial and final states of the ion. We separate out in (34.1) and (34.2) the dependence on the nuclear charge $Z$. The functions $\psi_{A_0}$ and $\psi_A$ contain the quantity

$$\rho = Zr \tag{34.3}$$

as an argument, while the normalizing factor is proportional to $Z^{\frac{3}{2}}$. Therefore, $V_{A_0A}$ may be written in the form

$$V_{AA_0} = ZU_{AA_0}(\rho) \tag{34.4}$$

The function $\varphi_A$ contains as its arguments the quantities $Z_0/k_A$ and $k_A r$ where $Z_0$ is the charge on the ion, i.e.

$$\varphi_A = \varphi_A\left(\frac{Z_0}{k_A}, k_A \cdot r\right) \tag{34.5}$$

If we now express $r$ in terms of $\rho$ in accordance with (34.3) and substitute

$$p = \frac{k}{Z} \tag{34.6}$$

we have

$$\varphi_A = \varphi_A\left(\frac{Z_0}{Z_{p_A}}, p_A\cdot\rho\right) \tag{34.7}$$

For hydrogen-like ions $Z_0 = Z-1$, so that

$$\varphi_A = \varphi_A\left(\frac{1-\frac{1}{Z}}{p_A}, p_A\cdot\rho\right) \tag{34.8}$$

Substituting (34.4) and (34.8) into (34.1) we have

$$q_{A_0A}(p_{A_0}, p_A) = -\frac{1}{2\pi Z^2}\int \tilde{\varphi}_A U_{AA_0}\varphi_{A_0}\,d\rho \tag{34.9}$$

The cross-section is then given by

$$d\sigma_{A_0A} = \frac{1}{4\pi^2}\frac{p_A}{p_{A_0}}\frac{1}{Z^4}|M|^2 d\Omega \tag{34.10}$$

where

$$M = \int \tilde{\varphi}_A\left(\frac{1-\frac{1}{Z}}{p_A}, p_A\cdot\rho\right)_{AA_0} U_{AA_0}\varphi_{A_0}\left(\frac{1-\frac{1}{Z}}{p_{A_0}}, p_{A_0}\cdot\rho\right)d\rho \tag{34.11}$$

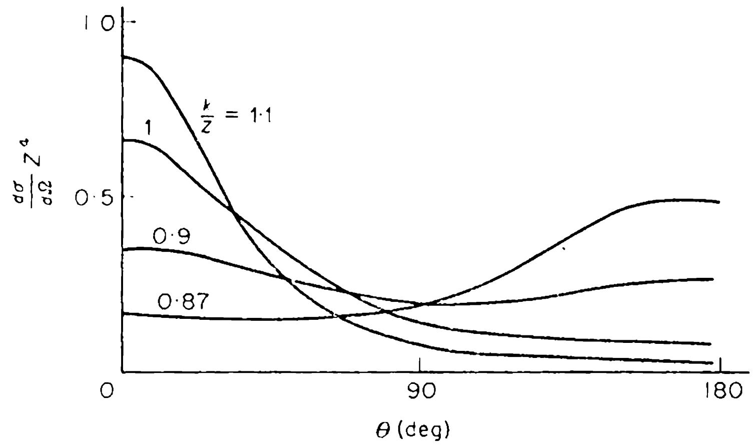

FIG. 47. Angular distribution of electrons in the case of the excitation of the $2s$-state of the helium ion

When $Z \gg 1$ we can neglect $Z^{-1}$ in the arguments of $\tilde{\varphi}_A$ and $\varphi_{A_0}$, and $M$ is then independent of $A$. According to (34.10) the cross-section is then inversely proportional to $Z^4$. The integration in (34.11) is carried out numerically. The angular distributions of the scattered electrons are anisotropic, and when the energy of the incident electron is close to threshold, the maximum of the angular distribution lies near 180°. As an example, Fig. 47 shows the angular distribution for $Z = 2$ and the $1s-2s$ transition at different energies. Figure 48 shows the total excitation cross-section (obtained by numerical integration of the differential cross-section) for the $1s-2s$ transition for different $Z$. The results of calculations using the Born approximation and the distorted wave approximation [99] are given for the five-fold ionized carbon atom. In the units chosen in Fig. 47 ($p = k/Z$ along the abscissa axis) all the thresholds for the excitation of the $2s$ state lie at the single point $p^2 = 0{\cdot}75$. We note that the excitation cross-section at the threshold is finite. The reason for this was discussed in § 23.

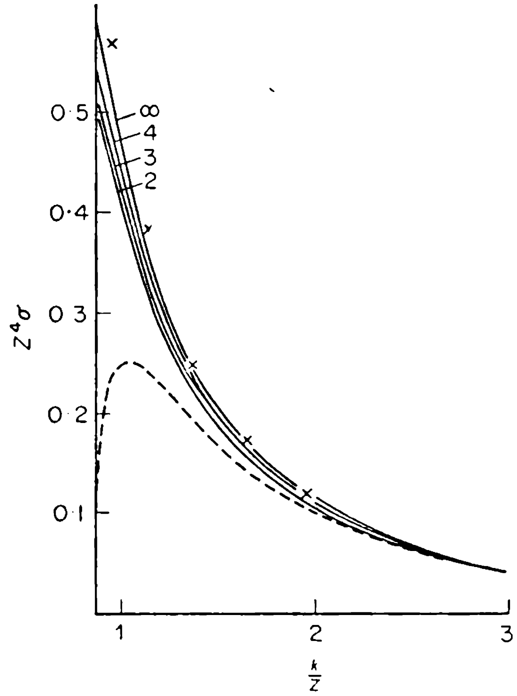

FIG. 48. Excitation cross-sections for the $2s$-state in hydrogenic ions of different nuclear charge: points—distorted wave approximation (in units of $\pi a_0^2$); broken curve—Born approximation

## 35. Optically Allowed Transitions on the Dipole Approximation

Let us consider now the excitation of optically allowed transitions. If we replace the matrix element $V_{AA_0}$ by its asymptotic expression for large $r$, we have

$$V_{AA_0} \sim \frac{r}{r^3} D_{AA_0} \tag{35.1}$$

where $D_{AA_0}$ is the matrix element for the dipole moment. The quantity $D_{AA_0}$ is in its turn related to the oscillator strength for the particular transition.

The excitation cross-section may be expressed in terms of the oscillator strength $s_{AA_0}$ as follows [98]:

$$\sigma_{A_0A} = \frac{s_{A_0A}}{(\Delta E)^2}\,\sigma_0\left(\frac{\Delta E}{Z^2}, \frac{E}{\Delta E}\right) \tag{35.2}$$

where $\Delta E$ is the transition energy, $E$ is the energy of the incident electron;

$\sigma_0$ is given by

$$\sigma_0\left(\frac{\Delta E}{Z^2},\frac{E}{\Delta E}\right)=2\pi^2\frac{\Delta E}{E}\frac{e^{2\pi\eta}}{(e^{2\pi\eta}-1)(e^{2\pi\eta'}-1)}x_0\frac{d}{dx_0}\left|F(i\eta,i\eta',1,x_0)\right|^2 \qquad (35.3)$$

where

$$\eta=-\frac{Z}{\sqrt{2\Delta E}}$$

$$\eta'=-\frac{Z}{\sqrt{2(E-\Delta E)}}$$

$$x_0=-\frac{4\eta\eta'}{(\eta'-\eta)^2} \qquad 35.4)$$

and $F$ is the hypergeometric function.

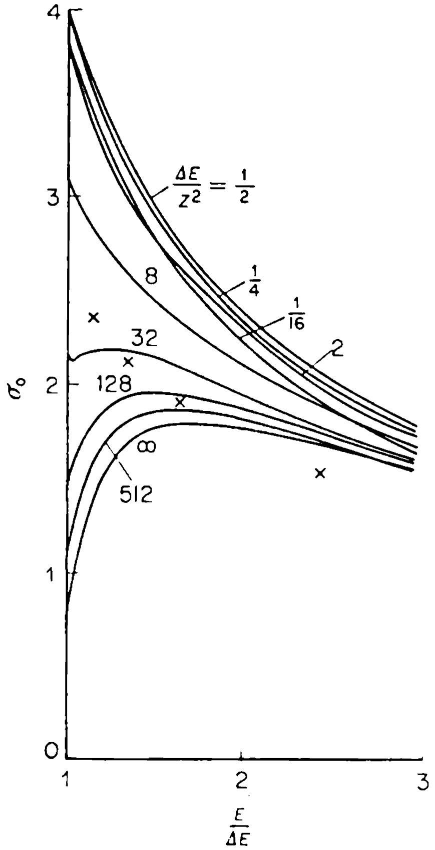

FIG. 49. A plot of $\sigma_0$ as a function of $E/\Delta E$ (points represent the distorted wave approximation)

Figure 49 shows $\sigma_0$ in units of $\pi a_0^2$ as a function of $E/\Delta E$ for different $\Delta E/Z^2$. This figure also shows $(\Delta E)^2\sigma_{A_0A}/s_{A_0A}$ calculated from the data in [99], which gives the calculated cross-section for the transition $1s-2p$ in five-fold ionized carbon ions using the distorted wave approximation. A detailed table of $\sigma_0$ for different values of the arguments is given in [98].

# CONCLUSION

THE account presented in this book is in some respects incomplete. This is unavoidable because the theory of electron-atom collisions is in the process of rapid development, and in many cases only preliminary results are available. Nevertheless, it is possible to discern general trends in the development of the subject, and this enables us to indicate certain problems which will remain of current interest.

Firstly, we must mention the general analysis of cross-sections near threshold with allowance for coupling between channels and for polarization of the atom. Studies of resonances in the excitation cross-section for a particular atomic state near the excitation threshold for the next state (with higher energy) are of particular interest. The M-matrix formalism is convenient in such investigations (Section 12). Secondly, we must recall studies of the asymptotic behaviour of the wave function for the $p + e + e$ system when both electrons are in the continuous spectrum. This is necessary for the elucidation of the ionization cross-section near threshold. Calculations of cross-sections for the elastic and inelastic scattering of electrons by hydrogen atoms show that partial waves with large L play an appreciable part even relatively near threshold. As indicated in [61], the development of approximate methods of calculation which do not require the partial wave expansions will be of major importance in this connection.

In calculations of cross-sections for the scattering of electrons by complicated atoms, one encounters the unavoidable problem of the rational choice of approximate atomic functions, and also the problem of the general structure of expressions describing the electron-atom interaction when approximate atomic functions are employed (this was considered in Section 26 in connection with the form of the exchange operator).

Among the current problems in collision theory, there is the development of approximate formulae for estimating the cross-sections (possibly with the aid of some experimentally obtained parameters), and also approximate formulae which are convenient in the integration of the velocities of the incident electrons over the spectrum. Simple formulae of this nature may be obtained on the basis of classical mechanics. In this connection we must mention the work reported in [100] and [101].

Finally, the successful application of the methods of quantum field theory in a number of branches of theoretical physics suggests that the introduction of these methods into the theory of atomic collisions will turn out to be fruitful.

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